CHELATED TRACE MINERALS IN RUMINANT NUTRITION

by

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In recent years a considerable number of claims have been made regarding the physiological effects of supplementing ruminant diets with trace mineral chelates or complexes. The organic trace mineral supplements commercially available vary in regard to the type of ligand or ligands used to form the metal complex or chelate. Organic minerals marketed are classified as complexes, chelates or proteinates. Definitions given by the Association of American Feed Control Officials for the various types of organic mineral products are shown in table 1.

TABLE 1. Definitions of Various Organic Mineral Products According to the Association of American Feed Control Officials[a]

T57.150 Metal amino acid complex - The product resulting from the complexing of a soluble metal salt with an amino acid(s).
57.142 Metal amino chelate - The product resulting from the reaction of a metal ion from a soluble metal salt with amino acids with a mole ratio of one mole of metal to one to three (preferably two)moles of amino acid to form coordinate covalent bonds. The average weight of the hydrolyzed amino acid must not exceed 800.
67.23 Metal proteinate - The product resulting from the chelation of a soluble salt with amino acids and/or partially hydrolyzed protein.
57.29 Metal polysaccharide complex - The product resulting from complexing of a soluble salt with a polysaccharide solution declared as an ingredient as the specific metal complex.

[a]From Patton, 1990.

Chelation refers to a special type of complex formed between a ligand and a metal ion. To be classified as a chelate the ligand or chelating agent must: 1) contain a minimum of two functional groups (oxygen, nitrogen, amino, hydroxyl) each capable of donating a pair of electrons to combine (via coordinate covalent bonding) with the metal and 2) form a heterocyclic

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ring structure with the metal (Kratzer and Vohra, 1986). Not all metal complexes are chelates.

Trace metals in blood and other tissues and trace minerals naturally occurring in feedstuffs exist largely bound to various ligands as organic complexes or chelates rather than as free ions. In contrast trace minerals have usually been supplemented to animal diets as inorganic salts. The development and marketing of trace mineral complexes or chelates has centered around the theory that they supply a more bioavailable mineral or a form of the trace mineral more similar to that naturally occurring in the body than inorganic sources. If the metal complex or chelate is stable in the digestive tract, the metal would be protected from forming complexes with other dietary components that inhibit absorption and thus, allow for greater absorption. This assumes that the metal complex or chelate can be absorbed as such or can be modified to a chemical form of the mineral that can be absorbed.

This paper will review the bioavailability of minerals in trace mineral chelates, proteinates and complexes and the effects of feeding these mineral sources on physiological responses in ruminants.

Proteinates

Proteinate forms are commercially available for copper, cobalt, iron, manganese and zinc. Metal proteinates are chelated minerals. Published results with metal proteinates are limited. Relative availability of manganese from manganese proteinate was similar to manganese sulfate in chicks fed diets either devoid of or containing fiber and phytate (Baker and Halpin, 1987). In this study manganese availability was assessed using bone and bile manganese concentrations in chicks fed high levels (1,000 ppm) of manganese.

Copper bioavailability in ruminants can be very low, primarily because of interactions with molybdenum and sulfur in the rumen. When dietary molybdenum and/or sulfur are high, providing copper in a form that would be stable in the rumen and not interact with these elements but be available for absorption in the small intestine would be advantageous. Two studies (Kincaid et al., 1986; Wittenberg et al., 1990) have compared the proteinate and sulfate forms of copper in cattle fed high molybdenum and the results obtained have been contrasting.

Kincaid et al. (1986) compared copper proteinate and copper sulfate in terms of their ability to increase copper status in calves (> 12 weeks old initially) fed a hay-concentrate diet naturally high in molybdenum. The basal diet contained 2.8 ppm of copper and 3.1 ppm of molybdenum. After 84 days calves given 26 mg of copper per day from copper proteinate had higher plasma (.87 vs .75 mg/l) and liver (325 vs 220 ppm) copper concentrations than calves supplemented with a similar level of copper from the sulfate form. Copper sulfate did not increase plasma or liver copper above values observed in non-copper-supplemented calves. However, control calves were not deficient in copper at the end of 84-day study based on liver and plasma copper concentrations and calf gains were not affected by copper level or source. These results suggested that absorption of copper from the proteinate form was less affected by high molybdenum.

Recently, Wittenberg et al. (1990) published the results of two studies which indicated

that availability of copper in copper proteinate and copper sulfate was similar in copper-depleted steers fed diets containing high molybdenum. A summary of their findings is presented in table 2. In both experiments steers were depleted of copper prior to the start of the study by feeding a diet supplemented with 100 ppm of molybdenum and .3 to .4% sulfur for 35 to 42 days. Steers were fed corn silage-barley based diets supplemented from 10 ppm of molybdenum in both experiments. Copper was supplemented to the basal diets to provide either 0 or 10 ppm added copper from the sulfate or proteinate form. Experiment 1 lasted 140 days and experiment 2 lasted 84 days. Liver and plasma copper values shown in table 2 are mean values of samples taken initially and at 35 (experiment 1) or 42-day (experiment 2) intervals. In both experiments plasma copper was increased by copper supplementation but plasma copper was not affected by copper source. Liver copper was not affected by copper level or source in experiment 1 but liver copper was increased by copper supplementation in experiment 2.

TABLE 2. Effect of Copper Proteinate and Copper Sulfate on Copper Status and Performance of Steers[a]

	Treatment		
	Control	Copper Sulfate	Copper Proteinate
Experiment 1			
Plasma Cu, μg/dl	33[b]	48[c]	52[c]
Liver Cu, mg/kg	12.5	15.6	15.9
Gain, kg/d	1.19[b]	1.29[b,c]	1.39[c]
Feed/gain	8.43	7.56	7.52
Experiment 2			
Plasma Cu, μg/dl	44[b]	61[c]	65[c]
Liver Cu, mg/kg	21.7[b]	34.0[c]	38.1[c]
Ruminal soluble Cu, μg/dl	41	53	74
Gain, kg/d	1.02	.98	1.01
Feed/gain	6.36	6.64	6.41

[a]From Wittenberg et al. (1990).
[b,c]Means in a row with unlike superscripts differ $P < .05$.

It is interesting to note that even though liver and plasma copper was not affected by copper source, steer gains were higher in steers receiving copper proteinate in experiment 1 but not in experiment 2 (Wittenberg et al., 1990; table 2). The proteinate diet in experiment 1 analyzed 20% higher in copper than the copper sulfate diet. Steer gains in experiment 1 appeared to respond to increased dietary copper. Therefore, it is not clear if the higher gain in

steers fed copper proteinate was simply due to higher dietary copper or to copper proteinate per se.

There are differences between the study conducted by Kincaid et al. (1986) and those conducted by Wittenberg et al. (1990) that may explain the contrasting results in regard to copper bioavailability from copper proteinate. Kincaid et al. (1986) compared the relative availability of copper from the proteinate and sulfate form in calves adequate in copper while Wittenberg et al. (1990) made similar measurements in steers deficient in copper. Calves used by Kincaid et al. (1986) also were much younger than the steers used by Wittenberg et al. (1990). Finally, Wittenberg added ammonium molybdate to increase dietary molybdenum while Kincaid used hay that was naturally high in molybdenum.

Chelates

Plasma zinc concentrations and alkaline phosphatase activity decreased greatly in lambs fed a zinc-deficient diet supplemented with only 5 ppm of zinc from either chelated (EDTA) or sequestered zinc (Ho and Hidiroglow, 1977). Lambs fed 5 ppm of chelated or sequestered zinc did not develop signs of zinc deficiency and gained similarly to lambs fed 50 ppm of zinc from zinc sulfate during a 42-day period. However, in zinc sulfate-fed lambs when dietary zinc was reduced from 50 to 5 ppm, signs of zinc deficiency were observed within 28 days (Ho and Hidiroglow, 1977).

Based on liver copper concentrations, no differences in relative availability of copper were observed between EDTA chelated copper and copper sulfate in steers fed a high molybdenum diet (Miltimore et al., 1978). Ashmead and Christy (1985) reported that in vitro uptake of iron, zinc and copper by intestinal tissue over a one-minute period was 1.7 to 4.9 times greater when the metal was presented as an amino acid chelate compared to an inorganic salt.

Gengelbach (1990) evaluated the effect of an amino acid-chelated mineral supplement on performance of beef cattle grazing endophyte infected tall fescue. Treatments consisted of free choice mineral supplements containing: 1) a combination of inorganic and amino acid chelated minerals, 2) inorganic minerals at levels equal to the levels present in supplement 1 and 3) a control mineral containing calcium, phosphorus and salt in the same levels as supplement 1 and 2 but no trace minerals. Seventy percent of the zinc, manganese and copper in supplement 1 was supplied as amino acid chelate. In a 168-day study with 36 growing steers, gains were similar in steers receiving the different mineral supplements. In a similar study with 96 beef cows and their calves, performance also was similar in cattle fed the three different mineral supplements (Gengelbach, 1990). A tendency ($P=.11$) was noted for cows that received the trace mineral supplements to have higher conception rates than cows that received no trace mineral supplementation. However, conception rates were similar in cows fed inorganic and chelated trace minerals.

In a study conducted at the University of Maryland, 40 first calf Holstein heifers were fed a control diet or the control diet plus an amino acid chelated mineral supplement (Manspeaker et al., 1987). Mineral content of the control diet was not reported. The amino acid chelated supplement supplied additional iron, manganese, copper and zinc in addition to

potassium and magnesium. The study was conducted from approximately 30 days prepartum until heifers were confirmed pregnant by rectal palpation. Incidence of periglandular fibrosis (a pathologic response in which endometrial tissue does not regenerate properly after parturition) was significantly lower (10 vs 58%) in heifers given chelated minerals. Although not statistically significant, ovarian activity tended to be higher and embryonic mortality lower for heifers fed the chelated mineral supplement.

Complexes

Metal complexes commercially available include zinc methionine, manganese methionine, iron methionine, copper lysine and cobalt glucoheptonate. Zinc methionine has been studied to the greatest extent of any of the chelated or metal complexes currently available. Cobalt glucoheptonate was developed to provide a source of cobalt readily available for uptake and utilization for vitamin B_{12} synthesis by ruminal microorganisms. Cobalt glucoheptonate and copper lysine will not be further discussed because no data have been published regarding their use in ruminant diets.

Zinc Methionine

Bioavailability. The methionine portion of zinc methionine has been shown not to be degraded to a large extent by ruminal microorganisms (Heinricks and Conrad, 1983). This suggests that the zinc methionine complex remains intact in the rumen and that the complex would potentially be presented to the small intestine as such.

Wedekind et al. (1990) found, using tibia zinc concentrations as a measure of availability, that relative availability of zinc in zinc methioinine was 177 to 206% compared to zinc sulfate. Based on plasma zinc, plasma alkaline phosphatase activity and animal performance, bioavailability of zinc from zinc methionine and zinc oxide was similar in lambs fed a semi-purified diet deficient in zinc (Spears, 1989). In this study, zinc was supplemented to the deficient diet at a level well below the lamb's requirement. Apparent absorption of zinc from zinc methionine and zinc oxide also was similar in lambs fed a semi-purified deficient diet or a hay-based diet (Spears, 1989). Urinary excretion of zinc tended to be lower in lambs fed zinc methionine. Following oral dosing with a high level of zinc from zinc methionine or zinc oxide, plasma zinc decreased to predosing baseline values at a slower rate in lambs given the methionine form. It was concluded from these studies that zinc in zinc oxide and zinc methionine was absorbed to a similar extent, but zinc from these two sources appeared to be metabolized differently following absorption (Spears, 1989).

Zinc uptake from zinc methionine and zinc chloride also was found to be similar using noneverted intestinal sacs from pigs and chicks (Hill et al., 1987). The amount of ^{65}Zn absorbed after 60 minutes from ligated rat intestine was less when labeled zinc was supplied from zinc methionine compared to zinc chloride (Hempe and Cousins, 1989). Studies that have been conducted have not provided a clear insight into what form zinc in zinc methionine is absorbed as.

Performance. A number of studies have evaluated the effect of zinc methionine on

performance of growing cattle or lactating dairy cows. Most of these studies have involved a control diet (containing a certain amount of added inorganic zinc) and the control diet supplemented with zinc methionine. An isozinc treatment has often not been included in the experimental designs. However, control diets have been formulated to contain or exceed NRC recommended levels for zinc.

Spears (1989) fed growing heifers a corn silage based diet containing 24 ppm of zinc or the basal diet supplemented with 25 ppm of zinc from zinc methionine or zine oxide. Average daily gain and feed efficiency were similar for control heifers and those supplemented with zinc oxide. Heifers receiving zinc methionine gained 8.1% faster ($P < .07$) and 7.3% more efficiently ($P < .08$) than control heifers for the entire 126-day study. Reproductive characteristics measured were similar across treatments.

An isozinc comparison between the oxide and methionine form of zinc also has been conducted with finishing steers (Greene et al., 1988). The basal diet used in this study contained 82 ppm of zinc and the addition of 360 mg of zinc from either source did not significantly improve performance for the entire 112-day study. However, quality grades, marbling scores and percent kidney, pelvic and heart fat were higher in steers fed zinc methionine compared to steers in the control or zinc oxide treatments. Improved quality grades in steers fed zinc methionine also have been observed in other studies (Brethour, 1984; Rust, 1985). In other studies with cattle (Carrica et al., 1986; Neal et al., 1986; Martin et al., 1987) and sheep (Stobart et al., 1987) zinc methionine did not affect carcass characteristics.

At least 19 feedlot studies have been conducted with zinc methionine by various universities and commercial feedlots (K. Ridenour, personal communication). A summary of the 19 trials is presented in table 3. With the exception of the 2 studies already described (Greene et al., 1988; Spears, 1989), all of these studies consisted of a control diet, formulated to meet or exceed NRC zinc requirements, and the control diet supplemented with zinc methionine. In most studies zinc methionine was added to supply 360 mg of supplemental zinc. Although most studies have not detected a significant performance response to zinc methionine, gain and feed efficiency have generally been numerically higher in cattle fed zinc methionine. Gains were numerically higher in cattle fed zinc methionine in 16 of the 19 trials and feed/gain ratios were numerically lower for zinc methionine fed cattle in 17 of the 19 trials. A pooled statistical analysis across all trials, using means from each experiment as a replication, indicated a significant improvement in gain ($P < .01$) and feed efficiency ($P < .01$) resulting from zinc methionine addition to the control diets. The mean, median and range for percent change in gain and feed/gain for the 19 trials in cattle fed zinc methionine compared to controls are shown in table 3. Median percent change was 3.2% for gain and 2.0% for feed/gain. This means that one-half of the 19 trials had percent gain improvements of greater than 3.2% and one-half had gain responses less than 3.2%.

Increased milk production and decreased somatic cell count have been observed in lactating dairy cows fed zinc methionine. Zinc methionine studies with lactating dairy cows were reviewed recently by Kellogg (1990). A summary of studies where milk production and somatic cell count have been measured in dairy cows fed a control or zinc methionine supplemented diet is presented in table 4. Control diets were formulated to contain zinc at levels equal to or

exceeding NRC requirements for lactating dairy cows. Zinc methionine was added to the control diets to provide from 180 to 412 mg of zinc. The 8 studies summarized ranged from 63 to 365 days in length. In 4 of the 8 dairy trials, zinc methionine significantly increased milk production (Aguilar and Jordan, 1990 ($P < .05$); Kellogg et al., 1989 ($P < .10$) or somatic cell count (Aguilar et al., 1988; Galton, 1990). However, many of the other studies have indicated trends for increased milk production and reduced somatic cell count. A pooled statistical analysis using each experiment as a replication indicated a significant ($P < .01$) improvement in milk production and somatic cell count.

TABLE 3. Summary of 19 Feedlot Trials With Zinc Methionine[a]

	Gain, kg/d	Feed/Gain
Control	1.38	7.04
Zinc Methionine	1.43	6.75
Percent change from control		
Range	-1.25 to 12.94	1.65 to -17.45
Mean	3.63	-4.12
Median	3.20	-2.00

[a]From Ridenour, personal communication.

TABLE 4. Summary of Zinc Methionine Studies with Lactating Dairy Cows[a]

	Milk Production kg/d	Somatic Cell Count x1000
Control	30.28	346
Zinc Methionine	31.73	246
Percent change from control		
Range	.68 to 7.04	-6.2 to -49.6
Mean	4.80	-28.9
Median	5.80	-22.0

[a]From Kellogg (1990).

We recently completed a 2-year study designed to determine if including zinc methionine and manganese methionine in a free choice mineral would affect performance of beef cows and their calves (Spears and Kegley, 1990). Treatments consisted of complete mineral supplements containing: 1) no supplemental zinc and manganese, 2) 2,500 ppm of zinc and manganese from the oxide forms and 3) 2,500 ppm of zinc and manganese (two-thirds from the methionine forms

and one-third from the oxide forms). The experiment started approximately 3 months prepartum and cows remained on the same treatment for both years unless they were culled. Sixty-six cows were used in year 1 and 60 cows were used in year 2. Cattle were fed corn silage and alfalfa haylage during the winter and grazed orchardgrass, bluegrass and white clover pasture during the growing season. Calf weaning weights adjusted for sex, age and MPPA scores of the dams are shown in table 5. Compared to the control treatment, weaning weights were higher ($P<.10$) for calves in the zinc and manganese methionine treatment in year 1, but not in year 2. Weaning weights were higher ($P<.05$) for zinc and manganese methionine calves compared to control calves when data were combined across both years. Interestingly, calves receiving the zinc and manganese oxide supplement tended to weigh less than controls at weaning in both years. Weaning weights of calves in the zinc and manganese methionine treatment were heavier than those in the oxide treatment in year 1 ($P<.05$) and year 2 ($P<.10$). It is not clear if the response in calf gains was due to zinc methionine, manganese methionine or the combination of the two metal complexes. Further studies are warranted in this area.

TABLE 5. Weaning Weights of Calves Receiving Zinc Methionine and Manganese Methionine in a Free-Choice Mineral

	Supplement		
	Control	ZnO,MnO	ZnMet,MnMet
Weaning Weights, kg[a]			
Year 1	304.5	296.9	318.8
Year 2	255.7	251.6	261.6
$\bar{X}$	280.0[c]	274.1[c]	290.3[d]

[a]Adjusted for age, sex and MPPA scores of dams.
[c,d]Means in a row with unlike superscripts differ $P<.05$.

Immune Response and Disease Resistance. Zinc methionine also can affect immune responsiveness and disease resistance in ruminants. Spears et al. (1991) studied the effect of zinc level and source on performance and immune response in stressed steers that had recently been weaned and shipped. Steers were fed a control diet that contained 26 ppm of zinc or the control diet supplemented with an additional 25 ppm of zinc from either zinc oxide or zinc methionine. Performance was not significantly affected by treatment and morbidity rate was very low during the 28-day study. Antibody titers were determined on serum samples collected on days 0 and 14 as a measure of the immune response to bovine herpesvirus-1 (BHV-1) and parainfluenza$_3$ (PI_3) vaccination. Antibody titers against BHV-1 on day 14 following vaccination were 47 and 31% higher in steers supplemented with zinc methionine compared to control and zinc oxide fed steers, respectively.

Johnson et al. (1988) conducted five 28-day trials using a total of 773 newly received

calves to examine the effect of zinc methionine on health and performance. Calves were fed a control diet or the control diet supplemented with zinc methionine to supply 360 mg zinc/head/day. Zinc methionine supplemented calves gained 10.7% faster (.704 vs .636 kg/d), had a decreased morbidity rate (46 vs 51%) and required 5.8% fewer medical treatments (2.12 vs 2.25). Zinc methionine also reduced ($P < .03$) the required medical treatments per head (4.45 vs 4.94) for cattle that became sick during the studies. Data from calves detected as sick during the first 3 days of the studies were excluded.

Recently, we conducted two studies designed to determine the effect of feeding zinc methionine to calves prior to weaning on health and performance postweaning and shipping (Hutcheson and Spears, unpublished data). Calves were weaned in North Carolina and immediately shipped to Amarillo, Texas. Zinc methionine was compared to zinc oxide at an isozinc level and cattle received the same zinc source on arrival at the feedlot. In both studies calves fed zinc methionine gained faster during the postshipping period than those fed zinc oxide. Morbidity rate appeared to be lower (0 vs 20%) for zinc methionine supplemented calves in one of the two studies.

Zinc methionine has been recommended for prevention of foot-rot and other hoof problems based on field observations (Herrick, 1989). There is limited controlled research data to support this recommendation. Moore et al. (1988) reported that hoof growth and wear were similar in dairy cows fed a control and zinc methionine supplemented diet during a one-year study. However, they observed improved hoof scores for texture, heel cracks and interdigital dermatitis in zinc methionine fed cows. Incidence of foot-rot in finishing steers during a 112-day study was 20, 6.7 and 0% in control, zinc oxide and zinc methionine supplemented steers (Greene et al., 1988).

Manganese Methionine

Studies with chicks have indicated that manganese in manganese methionine is more available than manganese in the oxide (Fly et al., 1989) or sulfate form (Henry et al., 1989). Relative availability of manganese in manganese methionine was 174% of that present in manganese oxide based on bone manganese accumulation (Fly et al., 1989). Compared to manganese sulfate, relative availability of manganese in the methionine form was 108% based on bone and 132% based on kidney manganese concentrations (Henry et al., 1989). Chicks fed manganese methionine consumed slightly less feed and gained more ($P < .05$) efficiently than chicks fed equivalent amounts of manganese and methionine from manganese sulfate and DL-methionine (Henry et al., 1989).

Manganese methionine addition to diets of growing beef heifers improved gain and feed efficiency in one of two experiments (table 6). Manganese oxide did not affect performance in either experiment. In both studies heifers were fed corn silage and a protein-mineral supplement containing 0 or 20 ppm of supplemental manganese from either manganese oxide or manganese methionine. Supplemental crude protein in experiment 1 was supplied from a corn-urea supplement while approximately one-half of the supplemental protein in experiment 2 was provided from soybean meal and the other one-half from urea. Lack of a performance response to manganese methionine in experiment 2 may relate to the higher manganese content of the

basal diet especially the protein supplement. Part of the naturally occurring manganese in the soybean meal may have been present as manganese methionine or similar manganese complexes.

TABLE 6. Effect of Manganese Methionine on Performance of Growing Beef Heifers[a]

	Treatment		
	Control	Manganese Oxide	Manganese Methionine
Experiment 1			
Gain, kg/d	.60[b]	.62[b]	.67[c]
Feed/gain	12.5[d]	12.2[d]	11.2[e]
Manganese content, ppm			
Corn silage	17.9		
Protein supplement	7.8		
Experiment 2			
Gain, kg/d	.96	.96	.95
Feed/gain	9.7	9.7	9.6
Manganese content, ppm			
Corn silage	25.1		
Protein supplement	23.5		

[a]Spears, unpublished data; Studies were 140 days in length.
[b,c]Means in a row with unlike superscripts differ $P < .06$.
[d,e]Means in a row with unlike superscripts differ $P < .05$.

Conclusions

Under certain conditions ruminants respond (increased growth, milk production, reproduction, immune response, etc.) to certain trace mineral complexes or chelates. One cannot conclusively determine from many of the studies if the responses observed were due to the organic mineral(s) per se or simply to increased dietary mineral intake.

The mode of action of trace mineral chelates or complexes is largely unknown. For organic trace minerals to be beneficial it is reasonable to assume that they must be stable in the rumen environment (with the exception of cobalt complexes) and abomasum and be delivered to the small intestine intact. There is little evidence that trace mineral chelates or complexes are considerably better absorbed than inorganic forms based on apparent absorption or tissue and blood concentrations. Differences in absorption alone cannot justify the additional cost of the organic trace mineral in most instances because higher amounts of the inorganic trace mineral could be added to the diet at a lower cost. In explaining the beneficial responses to certain organic trace minerals the quantity of mineral absorbed may not be as important as the form of the mineral absorbed. Certain trace mineral chelates or complexes may stimulate certain

biological processes or the mineral present in the organic form may enter different pools within the body than inorganic forms.

Further research with trace mineral chelates and complexes is needed to: 1) better define conditions where performance or health responses may be expected, 2) determine the mode of action whereby organic trace mineral supplements improve animal performance and 3) determine if responses observed are of a magnitude necessary to justify the cost.

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