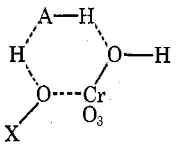
with respect to the nature of the incoming ligand, it is necessary to postulate that bond breaking is the most important feature of the activation process for eq 9, and therefore the reaction sequence is viewed as a dissociative mechanism in which the departure of the leaving group is facilitated by protonation.

To be sure, it is not possible to distinguish between the two mechanisms on the basis of the rate law, and this represents another example of ambiguities in mechanistic interpretations.[12] In the present case, the mechanistic ambiguity is ascribed to our inability to establish the order of aggregation of the three species required to define the composition of the activated complex for the reaction. However, for the particular system under scrutiny, it is possible to rule out the rate-determining proton transfer mechanism on the basis of phenomenological considerations related to diffusion-controlled reactions.[13] According to mechanism A, $k_f = k_0k_1/k_{-0}$. Since k_0 and k_1 are rate constants for diffusion-controlled processes ($\sim 10^{10}\ M^{-1}\ \text{sec}^{-1}$) and k_f is of the order of $5 \times 10^5\ M^{-2}\ \text{sec}^{-1}$, we calculate a value for k_{-0} of $\sim 2 \times 10^{14}\ \text{sec}^{-1}$, and therefore a lifetime of $\sim 5 \times 10^{-15}$ sec for the complex $XCrO_3OH^-$. Even allowing for a possible electrostatic repulsion between X and CrO_3OH^-, such a lifetime is approximately 4 orders of magnitude smaller than the lifetime of an encounter complex.[14] Consequently, the proposed[4] assignment of rate constants is rejected because it predicts a physically impossible value for k_{-0}.

Mechanism A can be modified, still retaining the feature of rate-determining proton transfer to $XCrO_3OH^-$, by decreasing the rate constant for the formation of the pentacoordinate species in eq 5 in order to obtain a physically permissible value for k_{-0}. Using $k_1 = 10^{10}\ M^{-1}\ \text{sec}^{-1}$ and $k_{-0} < 10^{11}\ \text{sec}^{-1}$, we calculate a value of $k_0 < 5 \times 10^4\ M^{-1}\ \text{sec}^{-1}$. However, even in this modified form, the mechanism does not seem satisfactory. The observed rate constant k_f has a contribution of the equilibrium constant k_0/k_{-0} for the *nucleophilic addition* of the incoming ligand to the Cr(VI) center to produce the pentacoordinate intermediate $XCrO_3OH^-$. With a tetracoordinate Cr(VI) center that covers a range of almost 10^7 in its thermodynamic affinity toward various nucleophiles, it does not seem reasonable that the corresponding pentacoordinate Cr(VI) center would not display some discrimination for the nucleophiles. On the basis of these considerations, we tend to discount mechanism A.

An alternate assignment of rate constants in mechanism A is $k_f = k_0k_1k_2/k_{-0}k_{-1}$ and $k_r = k_{-2}$. In this interpretation, the pentacoordinate intermediate $XCrO_3OH_2$ is in rapid equilibrium with H^+, X^-, and CrO_3OH^-, and loss of water from the intermediate is rate-determining. Again, the equilibrium constant k_0/k_{-0} for the nucleophilic addition of X^- to the Cr(VI) center is included in the observed rate constant k_f, and therefore the argument advanced against the first modification of mechanism A is still valid.

The dissociative mechanism B accounts nicely for the specific acid catalysis, but leaves unanswered the question of the general acid catalysis observed for $H_2PO_4^-$,[15] $H_2PO_3^-$,[16] and $HCrO_4^-$.[17] However, it must be noted that although general acid catalysis requires a rate-determining proton transfer for the path catalyzed by a general acid, the corresponding hydrogen ion catalyzed path need not be limited by proton transfer. An attractive pathway to account for the general acid catalysis involves a concerted mechanism whereby loss of OH^- from CrO_3OH^- and loss of H^+ from XOH^- ($X = PO_3H, PO_2H, CrO_3$) are assisted by the general acid HA by means of the cyclic transition state[17]



$X = PO_3H, PO_2H, CrO_3$
HA = general acid

Finally, it is noteworthy that the kinetic and free energy relationships observed in the Cr(VI) system are exactly parallel in the N(III) system[18] (X is a halide or thiocyanate)

$$HNO_2 + H^+ + X^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2O + XNO \qquad (10)$$

The rate low for the formation of XNO is given by $k_f[H^+][HNO_2][X^-]$. Moreover, the equilibrium constants for formation of ClNO and NCSNO differ by a factor of *ca.* 10^5, whereas the corresponding values of k_f differ by less than a factor of two. The mechanism proposed[18] to account for the substitution reactions on N(III) is given by eq 11 and 12. With the proviso that

$$ONOH + H^+ \rightleftharpoons ONOH_2^+ \ \text{Rapid} \qquad (11)$$

$$X^- + ONOH_2^+ \rightleftharpoons XNO + H_2O \ \text{Rate determining} \qquad (12)$$

bond breaking is the most important feature of the activation process in reaction 12, this mechanism is identical with the one proposed above to account for the observations on the substitution reactions of $HCrO_4^-$.

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[12] A. Haim, *Inorg. Chem.*, **5**, 2081 (1966).

[13] I. Amdur and G. G. Hammes, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1966, p 59.

[14] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 496.

[15] S. A. Frenesson, J. K. Beattie, and G. P. Haight, *J. Amer. Chem. Soc.*, **90**, 6018 (1968).

[16] S. A. Frenesson, J. K. Beattie, and G. P. Haight, *Acta Chem. Scand.*, **23**, 3277 (1969).

[17] R. Baharad, B. Perlmutter-Hayman, and M. A. Wolff, *J. Phys. Chem.*, **73**, 4391 (1969).

[18] D. E. Klimek, B. Grossman, and A. Haim, *Inorg. Chem.*, in press.

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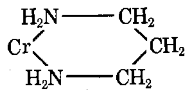
RECEIVED JUNE 12, 1972

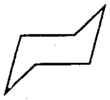
Conformations of Six-Membered Rings in Tris Metal Complexes. A Skew-Boat Conformation in $[Cr(NH_2CH_2CH_2CH_2NH_2)_3]^{3+}$

Sir:

The conformational problem presented by complexes containing six-membered chelate rings is similar to that posed by cyclohexane. For the ring system



the Cr–N bond of 2.08 Å is longer than a C–N or C–C bond, but the N–Cr–N angle of approximately 91° is less than that for C–C–C of 109° and these differences partially cancel one another. As a result, we may discuss the conformation of these six-membered chelate rings using the same language that has evolved from consideration of the cyclohexane conformers. We therefore expect the "chair" form (i) to be most stable,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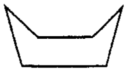
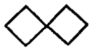

ii


iii

the "boat" form (ii) to be least stable, and an intermediate "skew-boat" or "twist" form (iii) to be slightly more stable than the boat. To our knowledge, every structure reported to date for a free cyclohexane ring system, including chelate rings, has reported a chair conformation.

The conformations of five-membered chelate rings in metal complexes have been extensively studied.[1] The relative stabilities of conformers have been calculated from intramolecular interatomic nonbonded interactions in the complexes and each of the four possible conformations for M(en)$_3$ complexes has been observed in the solid state.[2-4] In contrast, the relative stabilities of the possible conformations assumed by tris complexes of six-membered rings are not yet known and only one conformation has been observed previous to this report. There are several pronounced differences in the conformations of five- and six-membered chelate rings. The ring–ring interactions, which give rise to the energy differences between conformations, are more severe and more numerous in the six-membered chelate ring complexes than in five-membered systems.

In the following discussion of the various possible conformations of tris six-membered chelate ring systems a concise system of naming will be necessary. Such a nomenclature exists for five-membered rings,[5] but none that is applicable exists for six-membered chelate ring systems. There are four possible conformations for the tris ethylenediamine complexes. In contrast, if only the chair and twist conformations for six-membered rings are considered, we shall show that there are 16 possible conformations for tris(1,3-propanediamine) chelates.

Nomenclature for Conformations of Tris Chelate Complexes Containing Six-Membered Rings.—The IUPAC principles are incorporated into the nomenclature for tris chelate complexes containing six-membered rings whenever it is possible. For instance, the name of the overall configuration about the six-coordinate metal ion is Λ if the lines joining the ligators of the chelate and atoms adjacent to the ligators form a left-handed helical system. For a right-handed helical system, Δ is used.

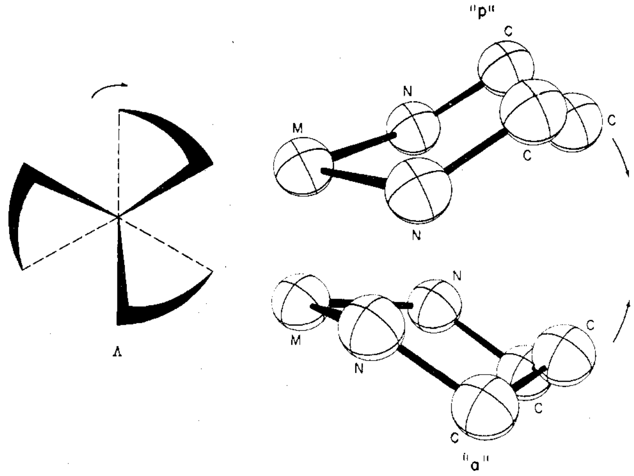


Figure 1.—Perspective drawings of the two chair conformers of 1,3-propanediamine rings. The upper ring is the "p" conformer and the lower ring is the "a" form.

The chair form of a six-membered chelate ring is not chiral and so there is no basis for its name in the recent IUPAC proposal.[5] However the interaction of such nonchiral rings with the metal center generates chirality and it is therefore necessary to specify the ring orientations. When viewed down the coordination axis, it can be seen from Figure 1 that there is a unique rotational direction defined by the metal ion configuration (clockwise in the figure, with a Λ configuration). The chair ring conformers may then fold such that the central carbon atom defines a rotation direction parallel to the direction defined by the metal ion configuration (as in the upper ring of Figure 1) or antiparallel (as in the lower ring). We designate these two conformations as p and a, respectively. The fold direction is determined by the orientation of the C–C–C plane. A twofold rotation perpendicular to the C_3 axis (this is the C_2 axis when the point group is D_3) interconverts these orientations, such that

$$\mathrm{p} \xrightarrow{C_2} \mathrm{a}$$

The skew-boat or twist conformer is chiral and its conformation within the complex can be defined based on the IUPAC proposal.[5] The notation for the skew-boat ring is the same as for ethylenediamine rings. The δ-ring conformation is that in which a line between the nitrogen atoms and a line between the carbon atoms bound to the nitrogen atoms defines a right-handed helix. (The ring in Figure 2 is in the δ-skew-boat conformation.) For a Λ configuration about the metal and a δ-ring conformation, the three carbon atoms define a plane which is approximately parallel to the coordination threefold axis. Similarly, for a Λ metal configuration and λ-ring conformation the plane of the three carbon atoms forms an obtuse angle with the coordination threefold axis. Both the δ- and λ-ring conformations have only one unique orentation such that

$$\delta \xrightarrow{C_2} \delta \quad \text{and} \quad \lambda \xrightarrow{C_2} \lambda$$

A twofold rotation of the molecule interconverts two rings and also transforms the chair conformers. If the

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[1] For a recent comprehensive review, see J. K. Beattie, *Accounts Chem. Res.*, **4**, 253 (1971), and references cited therein.

[2] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968).

[3] K. N. Raymond and J. A. Ibers, *ibid.*, **7**, 2333 (1968).

[4] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, **7**, 842 (1968).

[5] Proposed IUPAC Convention, *ibid.*, **9**, 1 (1970).

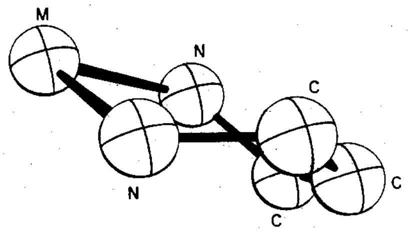

Figure 2.—A perspective view of the "∂" skew-boat conformer.

Table I

Possible Conformations of Tris Complexes of Six-Membered Chelate Rings

Conformer[a]	Symmetry	Conformer	Symmetry
Λppp	C_3	Λp∂λ	C_1
Λppa	C_1	Λpλa	C_2
Λpp∂	C_1	Λpλ∂	C_1
Λppλ	C_1	Λpλλ	C_1
Λpa∂	C_2	Λ∂∂∂	D_3
Λpaλ	C_2	Λ∂∂λ	C_2
Λp∂a	C_2	Λ∂λλ	C_2
Λp∂∂	C_1	Λλλλ	D_3

[a] Examples of enantiomorphic pairs are Λppa and Δppa, Λpa∂ and Δpaλ, and Λ∂λλ and Δλ∂∂.

twofold is taken to pass through the third ring (λ in this example), transformations such as the following result

$$\Lambda p\partial\lambda \xrightarrow{C_2} \Lambda\partial a\lambda$$

The twofold rotation also reverses the direction of the coordination threefold axis so that the top view of one conformation along the coordination threefold axis is the bottom view of the twofold related conformation. The threefold operation simply permutes the rings and does not affect the direction of the threefold axis. The following transformations result

$$\Lambda p\partial\lambda \xrightarrow{C_3} \Lambda\lambda p\partial \xrightarrow{C_3} \Lambda\partial\lambda p$$

When these symmetry operations are exhaustively applied to the 64 possible combinations and permutations of conformations, *only 16 unique* conformers result. The 16 unique conformations and their molecular symmetries are given in Table I. The first ring named in the molecule uniquely determines what is the top and what is the bottom of the conformation. The order for naming the conformations is p, a, ∂, λ. The next ring named is clockwise to the first if the metal ion configuration is Λ and counterclockwise for a Δ configuration (that is, the direction determined by the chirality of the complex). Note that these complexes formed from six-membered chelate rings can have D_3 symmetry only if all three rings assume a twist conformation. If the chair conformation is present, the highest possible symmetry is C_3 and the top and bottom of the complex are very different.

Conformational Studies.—The first conformational analysis of six-membered chelate ring systems appears to be that of Woldbye, who predicted that three 1,3-propanediamine rings coordinated to one Co^{3+} ion would each assume the skew-boat conformation in order to minimize the very serious hydrogen–hydrogen interatomic repulsions between rings.[6] In our notation, this prediction is that the Λ∂∂∂ conformer should be lowest in energy. This prediction has also been made by Butler and Snow, who calculate a difference in energy between the Λppp and Λ∂∂∂ conformers of 0.77–0.9 kcal/mol.[7,8] Gollogly and Hawkins, however, calculated a free energy difference of 0.9 kcal/mol between the Λ∂∂∂ and the Λppp conformers in $[Co(tn)_3]^{3+}$.[9]

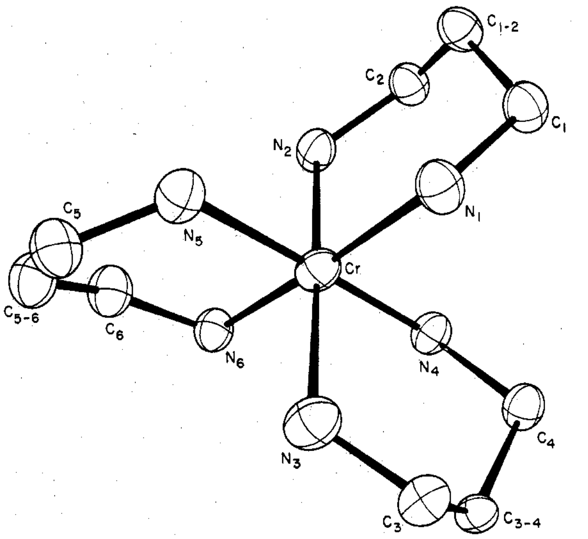

Figure 3.—A perspective view down the coordination threefold axis of the $[Cr(tn)_3]^{3+}$ cation in $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$.[10] Starting with the lower right ring and moving clockwise, the rings are referred to as ring 1 ("p" conformer), ring 2 ("∂" conformer), and ring 3 ("a" conformer).

Neither of the previous studies considered the possibility of conformations composed of mixtures of chair and skew-boat rings. Gollogly and Hawkins explicitly ruled out all such conformations as being impossibly high in energy.[9] However, our recent characterization of a mixed skew-boat and chair conformation (Λp∂a) in the salt $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$ demonstrates that these conformations cannot be ignored.[10] The only other structure determination of a tris(1,3-propanediamine) complex is that by Saito for (−)D-$[Co(tn)_3]Br_3\cdot H_2O$.[11,12] The cation in that case has nearly trigonal symmetry with all three rings in the chair form. The absolute configuration and conformation is then Λppp. Hayes, Parris, and Busch have calculated the relative thermodynamic stabilities of 13 of the 16 possible conformations. Although one of the three for which calculations were not successful was the Λp∂a conformer, these authors found that entropy effects favor the mixed skew-boat conformations and significantly lower their relative free energy.[13]

The $[Cr(tn)_3]^{3+}$ Cation in $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$.—In $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$ only two of the 1,3-propanediamine rings have the expected chair conformation.[10] It is clear from stereoscopic drawings and dihedral angles that the third ring forms the conformationally less stable twist or skew-boat conformer. The average dihedral angles of 79.0° between the planes Cr–N_5–C_5 and N_6–C_6–C_{5-6}, and between the Cr–N_6–C_6

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[6] F. Woldbye, "Studies on Optical Activity," Polyteknish Forlag, Copenhagen, 1969, p 210.

[7] R. J. Geue and M. R. Snow, *J. Chem. Soc. A*, **19**, 2981 (1971).

[8] K. R. Butler and M. R. Snow, *Inorg. Chem.*, **10**, 1838 (1971).

[9] J. R. Gollogly and C. J. Hawkins, *ibid.*, **11**, 156 (1972).

[10] F. A. Jurnak and K. N. Raymond, to be submitted for publication. A preliminary account of this structure was presented at the 162nd National Meeting of the American Chemical Society, Washington D. C., 1971, Sept. Abstract INOR-64.

[11] Y. Saito, T. Nomura, and F. Marumo, *Bull. Chem. Soc. Jap.*, **41**, 530 (1967).

[12] T. Nomura, F. Marumo, and Y. Saito, *ibid.*, **42**, 1016 (1969).

[13] (a) L. J. DeHayes, M. Parris, and D. Busch, private communication. (b) L. J. DeHayes, Doctoral Thesis, The Ohio State University, 1971.

and N_5–C_5–C_{5-6} planes, define the amount of twist present in the ring. The overall conformation of the cation is also unusual. Threefold rotational symmetry has been destroyed not only by the presence of a twist conformer but also by the direction of the fold of the remaining chair rings. In our notation the cation shown in Figure 3 is the $\Lambda p\partial a$ conformer. The complex therefore has an approximate twofold symmetry axis which relates the p and a rings and bisects the ∂ ring in passing through the central carbon of that ring.

The qualitative features of the conformational energy differences can be separated into two categories. In the first, the bond angle distortions of the ring are caused by inter-ring H–H nonbonded interactions between the amine and methylene hydrogens of neighboring rings. In the second category, the primary inter-ring repulsions are those between the amine hydrogens. Calculations by Snow indicate that the former type of repulsions causes a pronounced flattening of the ring.[7] Such an effect is observed in the two chair ring conformations where, in the absence of distortions, there would be pronounced H–H interactions between NH_2 and CH_2 groups. The average dihedral angles between the N–Cr–N and the N–C–C–N planes are 28.3 and 29.3° for the a and p chelate rings. The average Cr–N–C and N–Cr–N angles are 120.7 and 90.0°, respectively. The corresponding angles for the skew-boat ring are 116.6 and 89.2°. In the chair conformers the average N–C–C angle is 112.4° and the average C–C–C angle is 114.4°. In the skew-boat ring, the average N–C–C angle is 119.2° and the C–C–C angle is 117.2°.[14]

Unlike five-membered ring systems, an explanation for the observed conformations of the cation in $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$ is not found in the number and positions of hydrogen bonds formed.[10] In fact, the skew-boat ring forms fewer hydrogen bonds than do the chair rings in $[Co(tn)_3]Br_3\cdot H_2O$.[11,12] The skew-boat ring forms one more hydrogen bond, although very weak, than do the other rings. We conclude that the energy difference between the skew-boat and chair conformers ($\Lambda p\partial a$ and Λppp) must be exceedingly small in $[Cr(tn)_3]^{3+}$.

Acknowledgment.—This research was supported by the National Science Foundation through Grants GP-13278 and GP-29764 and by the Alfred P. Sloan Foundation through a Research Fellowship to K. N. R.

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(14) The original structure was determined at room temperature and was accompanied by crystal decomposition. A recollection of the X-ray diffraction data at low temperatures is in progress.

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RECEIVED JULY 3, 1972

Additions and Corrections

1971, Volume 10

William M. Butler and John H. Enemark: Chelative Addition of Hydrazine to Coordinated Isocyanides. The Structure of 1,1′-Dichloropallado-2,5-di(methylamino)-3,4-diazacyclopentadiene, $[(CH_3)_2C_2N_4H_4PdCl_2]$.

Page 2416. The name of the title compound should be 3,4*H*-1,1-Dichloro-2,5-di(methylamino)-1,3,4-palladodiazole.—J. H. ENEMARK

1972, Volume 11

J. W. Faller and M. J. Mattina: Organometallic Conformational Equilibria. IX. Isomerism and Hindered Rotation about Palladium–Nitrogen Bonds in π-Allyl Complexes.

Page 1307. The Acknowledgment was omitted: "Acknowledgment is made to the Connecticut Research Commission and to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research."—J. W. FALLER

Juan F. Villa and William E. Hatfield: Magnetic Studies on Amino Acid Complexes of Copper(II). II. Novel Interactions in Tetrakis(L-tyrosinato)dicopper(II).

Page 1331. Although adequate structural data were available to us [D. Van der Helm, private communication], we incorrectly depicted the structure of bis-L-tyrosinatocopper(II) as being dimeric when, in fact, the structure consists of infinite spiraling chains of copper(II) ions bridged by L-tyrosinate ligands. Since the epr spectrum gives evidence for a copper–copper interaction, and the magnetic susceptibility data indicate a ferromagnetic intrachain interaction, it seems clear that the correct explanation for the magnetic properties of bis(L-tyrosinato)copper(II) should be in terms of a ferromagnetic intrachain interaction with an antiferromagnetic interchain interaction becoming important at very low temperature. It is important to point out that the dimer equation (2) given on page 1333 gives a better fit of the magnetic susceptibility data than the Ising equations for chains which do not take interchain interactions into account. Although the coupling constant given in the original paper cannot be correct, the copper–copper interaction must occur by the superexchange mechanism suggested originally.—W. E. HATFIELD

M. D. Brice and B. R. Penfold: Structural Studies of Derivatives of Methinyltricobalt Enneacarbonyls. V. Crystal Structure of Bis(methinyltricobalt enneacarbonyl), $[CCo_3(CO)_9]_2$.

Page 1381. The first paragraph of the Introduction should read: "The compound $Co_6(CO)_{18}C_2$ was first reported by Bor, Markó, and Markó[2a] and was later prepared by an improved method[2b] by warming bromomethinyltricobalt enneacarbonyl, $BrCCo_3(CO)_9$, in toluene. It was assumed[2a] that it was a dimer containing two connected $-CCo_3(CO)_9$ units of the type first structurally characterized in $CH_3CCo_3(CO)_9$." Reference 2 should read: (2) (a) G. Bor, L. Markó, and B. Markó, *Chem. Ber.*, **95**, 333 (1962); (b) G. Allegra, E. M. Peronaci, and R. Ercoli, *Chem. Commun.*, 549 (1966).—B. R. PENFOLD

Phirtu Singh, David Y. Jeter, William E. Hatfield, and Derek J. Hodgson: Out-of-Plane Interactions in Parallel-Planar Copper(II) Dimers. The Structure and Magnetic Properties of Dibromobis(2-methylpyridine)copper(II).

Page 1657. Replace the last sentence of the abstract with the following sentence: "Despite the weakness of the bridging of the dimer, the complex exhibits an antiferromagnetic interaction with a singlet–triplet splitting of 5 cm^{-1}."—W. E. HATFIELD

R. C. Buckley and J. G. Wardeska: The Linkage Isomerism of Bridging Thiocyanate in Binuclear Complexes.

Page 1724. The last sentence of the first paragraph in the Experimental Section should read: "Solutions containing the aquopentacyanocobaltate(III) ion were prepared by treating a solution of $K_3[Co(CN)_5N_3]$[17] with equimolar amounts of sodium nitrite and trichloroacetic acid." The present sentence incorrectly states that *sodium nitrate* was used in the reaction.—J. G. WARDESKA