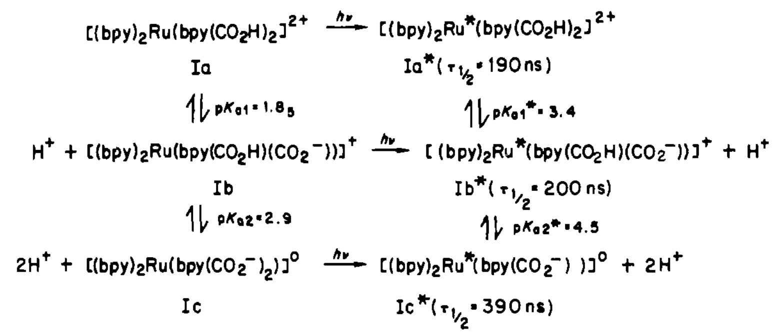
Scheme I



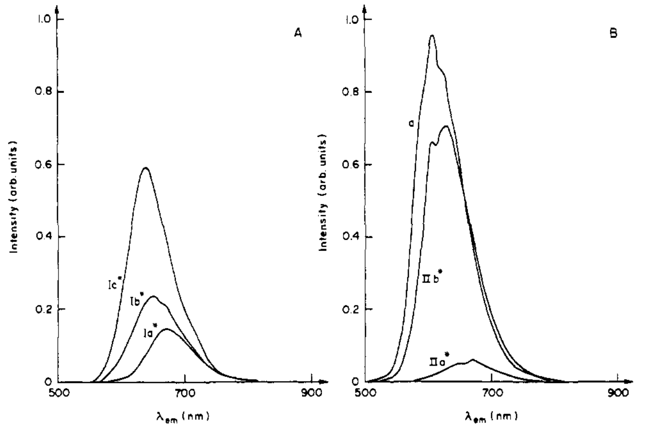


**Figure 2.** Uncorrected phosphorescence emission spectra: (A) Ia* (pH 1), Ib* (pH 3.95), Ic* (pH 13); (B) $[Ru^*(bpy)_3]^{2+}$ (a), IIa* (pH 1), IIb* (pH 13).

is also demonstrated by the pH dependence of the phosphorescence quantum yields. Two $pK_a^*$ values are evident ($pK_{a1}^* \sim 3.6$, $pK_{a2}^* = 4.5$), the first being manifested mainly in a broadening of the spectrum. The pH dependence of the lifetime of emission only showed the presence of the second $pK_a^*$ value. Figure 1 summarizes these results, giving $pK_{a1}^* = 3.6$ and $pK_{a2}^* = 4.5$ (cf., $pK_a^* = 8.8$ reported previously[1,15]), and Table I compares our results with previously reported data. The uncorrected emission spectra of the three excited states of I, which carry overall 2+ (Ia*), 1+ (Ib*), or no (Ic*) charges are given in Figure 2. While the uncorrected spectra show similar general characteristics to those reported previously,[1,3] they differ considerably in peak heights and emission maxima. Furthermore, large discrepancies in relative quantum yields, $pK_a$ values, and emission lifetimes were observed.[20] To check whether II may have been the source of these discrepancies, we measured its gound- and excited-state properties and obtained $pK_a$ values of comparable magnitude ($pK_a = 3.0$, $pK_a^* = 4.85$) to those observed for the diacid. Uncorrected emission spectra of the deprotonated complex IIb* and its acid form IIa* are shown in Figure 2; their photophysical properties are given in Table I. Probably, both the lack of correction of instrumental response and the presence of impurities account for the discrepancies between the present and earlier reported results.[1,3]

Clearly, the previous notion[1] that proton transfer is observed in the excited states of such molecules is correct; however, contrary to the reported results, we have now found that none, one, or two protons may be transferred, depending on pH. Thus, at pH ~3.1 one proton is transferred, while at pH ~4 two protons are transferred; these processes are summarized in Scheme I. One of the reviewers suggested that the $pK_a^*$ values observed may reflect the kinetics of protonation rather than the equilibrium situation. It was argued that protonation would have to be faster than the diffusion limit. However, proton transfer is not subject to diffusion control because protons can move through a hydrogen-bonded network by exchange, i.e., there is no need for the diffusion of a specific proton over extended distances. Moreover, if kinetic control were operating, one would expect to see changes near the second ground-state $pK_a$, as transfer of two protons would be required to maintain the same photophysical properties. Earlier work has shown that the electronic excitation energy of Ia* is localized on the $bpy(CO_2H)_2$ ligand[2] and that water effectively quenches the emission from ester derivatives.[20] This is likely to be the reason for the low phosphorescence yield and relatively short lifetimes of Ia*, Ib*, and IIa*, all of which possess one or two $CO_2H$ groups. The large shift in emission maximum of Ib* reflects of the relatively large change in the electron-withdrawing ability of the $CO_2H$ group, which occurs on deprotonation, and the broadness of the spectrum suggests that several well-separated triplet excited states are now contributing to the emission. In contrast, Ic* and IIb* have emission characteristics similar to those of $[Ru^*(bpy)_3]^{2+}$ where the splitting of the triplet excited states is expected to be smaller. In summary, the presence of a $-CO_2R$ substituent (R = alkyl, H) greatly reduces the quantum yields and lifetimes of emission, while the $-CO_2^-$ group has little effect. Details of quenching and hydrogen production experiments using these results will be presented elsewhere.[4]

**Acknowledgment.** P.A.L. gratefully acknowledges the receipt of a CSIRO Postdoctoral Fellowship. We also thank Dr A. W.-H. Mau for helpful comments on this paper.

**Registry No.** Ia, 62207-96-9; Ib, 72932-31-1; Ic, 64189-97-5; IIa, 92984-72-0; IIb, 93000-28-3.

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[20] Johansen, O.; Launikonis, A.; Mau, A. W.-H.; Sasse, W. H. F. *Aust. J. Chem.* **1980**, *33*, 1643–1648.

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## Factors Affecting the Metal-Promoted Head-to-Head Dimerization of $CS_2$ to $C_2S_4$. Synthesis, Chemistry, Structure, and MO Analysis of $[(triphos)Rh(\mu\text{-}C_2S_4)Rh(triphos)](BPh_4)_2\cdot CH_2Cl_2$

*Sir:*

The formation of a C–C bond between two stable molecules represents one of the most attractive goals of organometallic chemistry. Although most desirable would be a metal-promoted dimerization of carbon dioxide to give oxalate, encouraging results have been obtained by using carbon disulfide, a $CO_2$-like molecule. Indeed two examples of metal-activated head-to-head dimerization to form $C_2S_4$ species have been reported.[1,2] However, these reports do not provide any useful

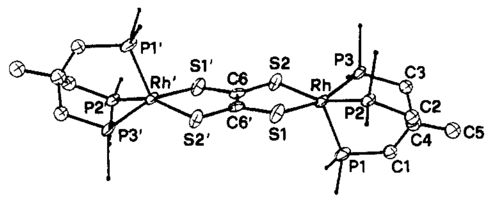

**Figure 1.** ORTEP drawing of the $[(\text{triphos})\text{Rh}(\mu\text{-}C_2S_4)\text{Rh}(\text{triphos})]^{2+}$ dimer. For the sake of clarity only the P–C(phenyl) vectors are shown. Distances: Rh–S1 = 2.310 (6), Rh–S2 = 2.295 (5), Rh–P1 = 2.245 (5), Rh–P2 = 2.309 (5), Rh–P3 = 2.334 (6), C6–S1′ = 1.76 (2), C6–S2 = 1.70 (2), C6–C6′ = 1.36 (3) Å. Angles: S1–Rh–S2 = 85.9 (2), P–Rh–P(av) = 89.2 (5)°.

hints for designing appropriate routes to C–C coupling of $CS_2$ or other related molecules. By contrast, the metal-promoted dimerization of $CS_2$ to $C_2S_4$, presented in this paper, sheds some light on the intrinsic mechanism of this type of reaction. On the basis of our experimental evidence, both the preliminary $\eta^2$-coordination of $CS_2$ to the metal and the presence of a Lewis acid in the reaction mixture seem to be, in fact, important requirements for achieving the dimerization to $C_2S_4$.

On addition of $CS_2$ to a THF/benzene solution of $[\text{RhCl}(C_2H_4)_2]_2$ and triphos (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane) in the presence of $\text{NaBPh}_4$, the color immediately turns deep green. Slow evaporation of the solvent yields quantitatively green crystals of the diamagnetic complex $[(\text{triphos})\text{Rh}(\mu\text{-}C_2S_4)\text{Rh}(\text{triphos})](\text{BPh}_4)_2$ (**1**).[3] Recrystallization of this product from $CH_2Cl_2$/ethanol affords crystals of formula **1**·$CH_2Cl_2$. In the absence of $\text{NaBPh}_4$, $CS_2$ reacts with the mixture of $[\text{RhCl}(C_2H_4)_2]_2$ and triphos to give red crystals of the diamagnetic complex $[(\text{triphos})\text{RhCl}(\eta^2\text{-}CS_2)]$ (**2**), yield 90%.[4] By treatment of solutions of **2** with Lewis acids such as $\text{HgCl}_2$, $BF_3$, $\text{HBF}_4$, and $\text{NaPF}_6$, complexes of formula $[(\text{triphos})\text{Rh}(\mu\text{-}C_2S_4)\text{Rh}(\text{triphos})]Y_2$ (Y = Cl, $BF_4$, $PF_6$) are formed. The metathetical reaction with $\text{BPh}_4^-$ anions then affords compound **1**. It is worthwhile to report that compound **2** remains unchanged when its solutions are treated under the same conditions with salts like $(\text{NBu}_4)\text{BPh}_4$.

Although studies are still under way, it is thus reasonable to suggest that the interaction of the Lewis acid with the exocyclic sulfur atom of the $\eta^2$-$CS_2$ group is responsible for the opening of the $\overline{\text{MCS}}$ ring. Hence, a possible mechanism for the formation of **1** implies the preliminary formation of **2** followed by the opening of the $\overline{\text{MCS}}$ ring. Rearrangement to the final complex **1** could be then achieved through the displacement of the chlorine atoms in two molecules of **2** by the originally uncoordinated sulfur atoms and the formation of a C–C bond. Support for this idea comes also from MO calculations, which indicate an easy interconversion between side-on and end-on coordination modes of $CS_2$.[5]

In the centrosymmetric structure of **1**·$CH_2Cl_2$[6] (Figure 1), two (triphos)Rh fragments are bridged by a $C_2S_4$ unit. Approximate $C_{2h}$ symmetry may be envisaged, with the twofold axis coinciding with the C(6)–C(6), bond and the orthogonal symmetry plane containing the P(1) and P(1)′ atoms. A displacement (0.30 Å) of the rhodium atoms from the $C_2S_4$ plane is suggestive of square-pyramidal geometry at each metal center. The Rh–P and Rh–S distances range between 2.245 (5) and 2.334 (5) Å and 2.295 (5) and 2.310 (6) Å, respectively. The values of the C–C and C–S bond lengths of 1.36 (3) and 1.73 (3) Å seem to indicate a formal ethenetetrathiolate nature of the bridging $C_2S_4$ group.

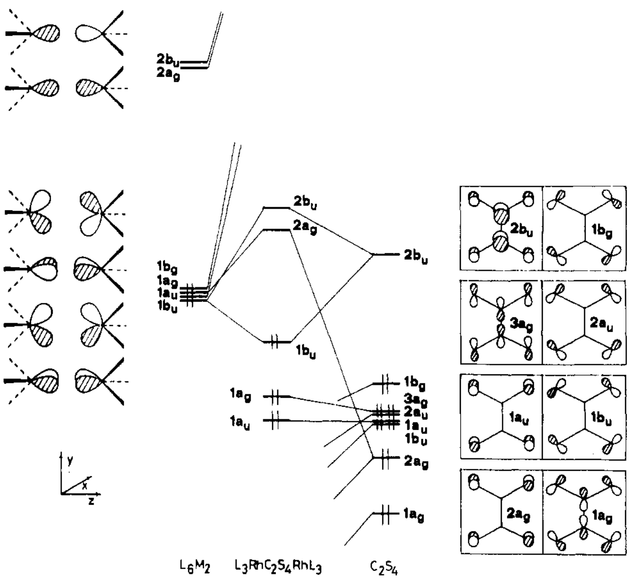

**Figure 2.** Diagram for the interaction between the orbitals of the $(PH_3)_6Rh_2$ and $C_2S_4$ fragments.

Interestingly, compound **1** undergoes redox chemistry that does not destroy its dimeric framework. In fact, **1** can be oxidized by $\text{NOBF}_4$ to give the red diamagnetic complex $[(\text{triphos})\text{Rh}(\mu\text{-}C_2S_4)\text{Rh}(\text{triphos})](BF_4)_4$ (**3**), whereas with $\text{LiHBEt}_3$ the brown paramagnetic complex with two unpaired electrons, $[(\text{triphos})\text{Rh}(\mu\text{-}C_2S_4)\text{Rh}(\text{triphos})]$ (**4**), is obtained. Both the formation of **3** and **4** from **1** are reversible; that is **1** can be re-formed from **3** and **4** by appropriate reducing or oxidizing agents, respectively.

In terms of the analogy between (triphos)M and CpM fragments,[8] then **1** has a comparable framework with that of the diamagnetic compound $[(C_5Me_5)\text{Ni}(\mu\text{-}C_2S_4)\text{Ni}(C_5Me_5)]$ (**5**) reported by Dahl et al.[2] It is noteworthy that **5** as well as the paramagnetic species **4**, obtainable from the reduction of **1**, contains two electrons more than **1**. It was previously suggested that a $\pi$ delocalization within the bridging $C_2S_4$ unit is an important feature of these systems.[2] Qualitative MO arguments supported by EHMO calculations[9] confirm this crucial point.

Figure 2 shows the main interactions between the known orbitals of the fragments $L_6M_2$[12] and $C_2S_4$.[13] There are four $\sigma$-bonding interactions in the plane of $C_2S_4$. Explicitly (referring to the orbitals of $C_2S_4$ and $L_6M_2$ in that order) these are $1a_g$–$2a_g$, $1b_u$–$2b_u$, $2a_u$–$1a_u$, and $1b_g$–$1b_g$. In every case the

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(1) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J., Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1982**, 140.

(2) May, J. J.; Rae, A. D.; Dahl, L. W. *J. Am. Chem. Soc.* **1982**, *104*, 4278.

(3) No IR bands in the C═S region are observed. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 293 K): doublet centered at 30.59 ppm ($J_{P-Rh}$ = 106.3 Hz). Molar conductance value ($10^{-3}$ M nitroethane solution): 98 Ω cm² mol⁻¹.

(4) IR (Nujol mull) (cm$^{-1}$): 1160 out-of-ring $\nu$(C═S); 640 in-ring $\nu$(C–S); nonelectrolyte.

(5) Mealli, C.; Hoffmann, R.; Stockis, A. *Inorg. Chem.* **1984**, *23*, 56.

(6) $[\text{Rh}(C_{39}H_{41}P_3)(CS_2)]_2[(C_6H_5)_4B]_2\cdot CH_2Cl_2$: (fw 2286.9) green parallelepiped shaped crystals, monoclinic, $P2_1/a$, $a$ = 15.496 (4) Å, $b$ = 28.736 (7) Å, $c$ = 14.216 (4) Å, $\beta$ = 106.02 (2)°, $V$ = 6084 (2) Å$^3$, $\rho_{\text{calcd}}$ = 1.248 g/cm$^3$ for $Z$ = 2. Solution and refinement of the structure were performed with SHELX76.[7] The present $R$ factors are $R(F)$ = 9.5% and $R_w(F)$ = 9.6% for 3195 independent data $[I \geq 3\sigma(I)]$ obtained via a Philips PW 1100 diffractometer with Mo K$\alpha$ radiation up to $2\theta$ = 50°.

(7) Sheldrick, G. M. "SHELX76"; University of Cambridge: Cambridge, England, 1976.

(8) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.

(9) The method is extended Hückel[10] with the FMO formalism.[11]

(10) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2872.

(11) (a) Hoffman, R.; Swenson, J. R.; Wan, C. C. *J. Am. Chem. Soc.* **1973**, *95*, 7644. (b) Fujimoto, N.; Hoffmann, R. *J. Chem. Phys.* **1974**, *78*, 1167.

(12) Dedieu, A.; Albright, T. A.; Hoffman, R. *J. Am. Chem. Soc.* **1979**, *101*, 3141.

(13) Gimarc, B. M. "Molecular Structure and Bonding"; Academic Press: New York, 1979; pp 187–192.

corresponding antibonding levels are too high in energy to be populated, so that the interactions can be regarded as the donation of four lone pairs from $C_2S_4$ to the metals.

The $L_6M_2$ orbitals $1b_u$ and $1a_g$ have $\pi_\perp$ symmetry as do the $C_2S_4$ $2b_u$ and $2a_g$ levels. The bonding–antibonding splitting of the $b_u$ species is enhanced on account of good energy match arguments. Since in both **1** and **5** the $2b_u$ antibonding combination is not populated, a net $\pi_\perp$ bonding interaction between $L_6M_2$ and $C_2S_4$ is created. If this is regarded as a back-donation from the metals (in every case the $C_2S_4$ $2b_u$ level lies at higher energy than the $L_6M_2$ partner and may be considered empty), the electron charge transferred into the C–C $\pi_\perp$ orbital ultimately forces the formation of a second bond between carbons (the C–C $\sigma$ bond may be envisaged as derived from the low $3a_g$ level of $C_2S_4$). The other $\pi_\perp$ interaction, of type $a_g$, is not as strong. Actually it is significantly stronger for rhodium[14] than for nickel,[15] mostly on account of a greater overlap between the interacting FMOs.[16] Thus, whereas in the case of nickel the MO $2a_g$ remains significantly lower than $2b_u$ (ca. 0.75 eV), in the case of rhodium the separation between these MOs is reduced remarkably (<0.3 eV). In summary $2a_g$ may be considered the HOMO in **5**, practically a metal-centered orbital. Conversely $2a_g$, destabilized by the antibonding interaction, is the LUMO in **1**, and a fifth lone pair may be considered donated from $C_2S_4$ to the rhodium metals. Finally, the vicinity of $2a_g$ and $2b_u$ levels, calculated for the rhodium model, rationalizes the high-spin state of **4**, whereas the above arguments justify the diamagnetism of the isoelectronic compound **5**.

Interestingly the analysis allows the description of both **1** and **5** as 18-electron species. Conversely, a simple count of the charges, when $C_2S_4$ is considered a tetraanion, would assign the formal oxidation state +3 to the metals in any case. This is very unusual for nickel and implies a description of rhodium centers as stable, nonplanar, 16-electron species. Instead, for **1** we propose $d^7$ metals that receive a total of 10 electrons from $C_2S_4$ and couple their unpaired electrons in a $\pi_\perp$ MO ($1b_u$) that ultimately forces a C=C double bond. In **5** two $d^8$ species receive only four pairs from the bridge, but the $\pi$ back-donation still occurs.

**Registry No.** **1**·$CH_2Cl_2$, 92669-50-6; **2**, 92669-51-7; **3**, 92669-53-9; **4**, 92669-54-0; [(triphos)Rh($\mu$-$C_2S_4$)Rh(triphos)]$Cl_2$, 92760-73-1; [(triphos)Rh($\mu$-$C_2S_4$)Rh(triphos)]$(BF_4)_2$, 92760-74-2; [(triphos)Rh($\mu$-$C_2S_4$)Rh(triphos)]$(PF_6)_2$, 92760-75-3; $CS_2$, 75-15-0; $[RhCl(C_2H_4)_2]_2$, 12081-16-2.

**Supplementary Material Available:** Listings of positional and thermal parameters for [(triphos)Rh($\mu$-$C_2S_4$)Rh(triphos)]$(BPh_4)_2$·$CH_2Cl_2$ (Tables I and II) and observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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(14) The parameters for rhodium were taken from: Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.

(15) The parameters for nickel were the same as in: Cecconi, F.; Ghilardi, C. A.; Innocenti, P.; Mealli, C.; Midollini, S. *Inorg. Chem.* **1984**, *23*, 922.

(16) Overlap values of 0.173 and 0.119 are calculated for the rhodium and nickel isostructural models. This difference certainly originates from the different diffuseness of the atomic orbital parameters utilized. However the difference may be even more pronounced in the actual complex **5**, for the terminal conical $(C_5Me_5)Ni$ fragments have frontier $\pi$ orbitals less hybridized than other isolobal $L_3Ni$ fragments.[8]

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## A Novel Isomer of *s-cis*-[Co(edda-type)(L)] (edda = Ethylenediamine-*N*,*N*′-diacetate; L = One Bidentate or Two Unidentate Ligands) Containing Equatorially Oriented N–$CH_2$ Bonds of the Acetate Arms. Crystal Structure of *s-cis*-[*N*,*N*′-Dimethyl-(1*R*,2*R*)-1,2-cyclohexanediamine-*N*,*N*′-diacetato](ethylenediamine)cobalt(III) Perchlorate, *s-cis*-[Co(*N*,*N*′-$Me_2$-*R*,*R*-chxnda)(en)]$ClO_4$

*Sir:*

The first X-ray structure determination of a novel *si-cis*-[Co(*N*,*N*′-$Me_2$-*R*,*R*-chxnda)(en)]$ClO_4$ (**1**) (*N*,*N*′-$Me_2$-*R*,*R*-chxnda = *N*,*N*′-dimethyl-(1*R*,2*R*)-1,2-cyclohexanediamine-*N*,*N*′-diacetate; en = ethylenediamine) containing the equatorially oriented N–$CH_2$ bonds of the acetate arms is reported.

A great number of metal complexes of ethylenediamine-*N*,*N*′-diacetate (edda) and related ligands have been isolated and characterized.[1] However, one of the fundamental s-cis isomers has long been excluded and is described in the following. For the *s-cis*-[Co(edda-type)(L)]$^n$, four isomers are theoretically possible as shown in Figure 1. In Figure 1, (a) and (b) and (c) and (d) are conformational isomers each other. When the central diamine ring of an edda-type ligand is fixed in a gauche conformation, the $\Delta$ and $\Lambda$ configurations are possible due to the orientation of the N–$CH_2$ bonds of the two acetate arms on the coordinated nitrogen atoms.[2] The isomer having the equatorially oriented N–$CH_2$ bonds of the acetate arms with respect to the central diamine chelate has long been excluded since the other isomer containing the axially oriented ones would be more preferred sterically.

The new *s-cis*-[Co(*N*,*N*′-$Me_2$-*R*,*R*-chxnda)(en)]$ClO_4$ was prepared by the oxidation of Co(II) to Co(III) in the presence of *N*,*N*′-$Me_2$-*R*,*R*-chxnda$H_2$, en, and activated charcoal.[6] The complex was recrystallized from warm water to give crystals suitable for X-ray analysis. Good elemental analyses were obtained.

The characterization of the complex as an s-cis isomer (the oxygen atoms are trans to each other) is based on its absorption and $^{13}C$ NMR spectra. The absorption spectrum[7] indicates that the complex (**1**) is a *trans*-$N_4O_2$ complex because of the shoulder in the first absorption region. The very simple $^{13}C$ NMR spectrum[8] suggests that the complex possesses the *trans*-$N_4O_2$ geometry with $C_2$ symmetry.

For tetragonal complexes of the type *s-cis*-[Co(edda-type)(L)]$^n$, the sign of the CD peak for the lowest energy $^1E$ transition is expected to be negative for a $\Delta$ configuration. [Co(*N*,*N*′-$Me_2$-*R*,*R*-chxnda)(en)]$^+$ shows a negative dominant CD peak and hence also might be expected to have the $\Delta$ configuration.[9]

From inspection of the scale models coupled with the spectroscopic results, the complex (**1**) in order to have the equatorially oriented N–$CH_2$ bonds of the acetate arms in the

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(1) Radanovic, D. J. *Coord. Chem. Rev.* **1984**, *54*, 159.

(2) These types of isomers have been reported about metal complexes of linear tetraamine tetradentate ligands as follows. Sargeson and Searle[3] discussed that similar isomeric possibilities arose from the absolute configurations of the coordinated secondary N atoms on $\beta$-cis [Co(trien)$X_2$], where trien = triethylenetetramine. Recently Shimura et al.[4] and Michelsen et al.[5] isolated and characterized independently the similar type of isomers due to the orientation of the N–$CH_2$ bonds on the secondary nitrogen atoms of Cr(III) complexes of *N*,*N*′-bis(2-pyridylmethyl)-1,2-propanediamine or its related ligands.

(3) Sargeson, A. M.; Searle, H. G. *Inorg. Chem.* **1967**, *6*, 787.

(4) Hata, Y.; Yamamoto, Y.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1255. Yamamoto, Y.; Shimura, Y. *Ibid.* **1981**, *54*, 2924.

(5) Michelsen, K.; Pederson, E. *Acta Chem. Scand. Ser. A* **1983**, *A37*, 141.

(6) The preparation and isolation will be dealt with in detail in a subsequent full paper.

(7) Absorption spectra (water) $\tilde{\nu}_{max}$, $cm^{-1}$ (log $\epsilon$): 18 330 (2.13), 19 800 (1.89), 26 670 (2.05).

(8) The complex shows only seven signals, which is consistent with s-cis geometry.

(9) CD spectra (water) $\tilde{\nu}_{max}$, $cm^{-1}$ ($\Delta\epsilon$): 17 000 (+0.30), 18 760 (−4.96), 26 250 (+0.80).

0020-1669/84/1323-4127$01.50/0