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 Δ and Λ 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 Δ 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 Δ 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).

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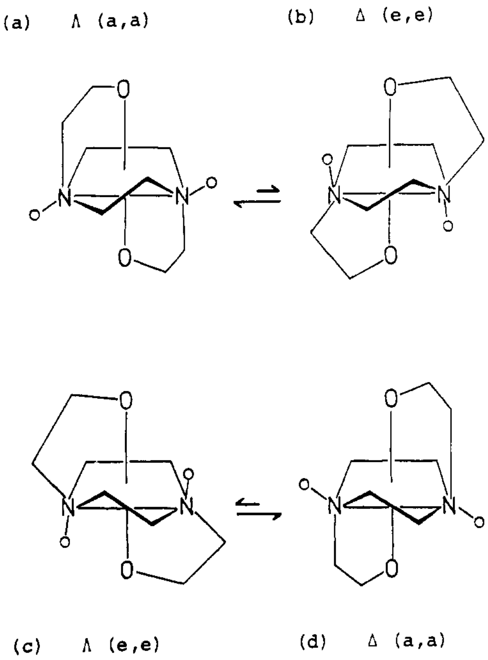

**Figure 1.** Possible isomers for *s-cis*-[Co(edda-type)(L)]$^n$. (e,e) and (a,a) indicate the equatorially oriented N–CH$_2$ bonds of the acetate arms and axially oriented ones, respectively.

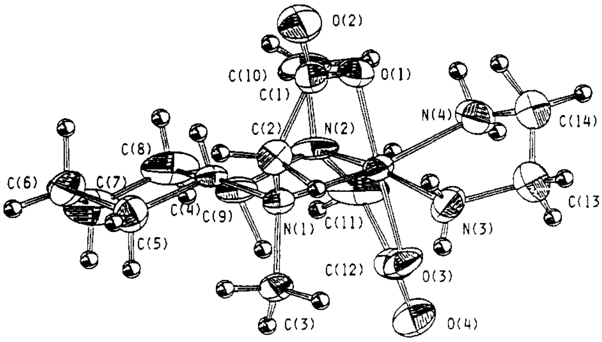

**Figure 2.** ORTEP drawing and atomic numbering scheme for the [Co($N,N'$-Me$_2$-$R,R$-chxnda)(en)]$^+$ ion. Important bond distances (Å): Co–O(1) = 1.891 (6); Co–O(3) = 1.890 (6); Co–N(1) = 1.972 (7); Co–N(2) = 1.990 (6); Co–N(3) = 1.995 (8); Co–N(4) = 1.973 (11).

central (1$R$,2$R$)-1,2-cyclohexanediamine ($R,R$-chxn) chelate was expected to adopt the stable λ conformation as shown in Figure 1b.

To confirm this structural prediction an X-ray crystal structure determination on the complex (**1**) has been undertaken.[10] Figure 2 shows the X-ray crystal structure of the complex cation. The geometry about the cobalt atom is distorted octahedral. The $N,N'$-Me$_2$-$R,R$-chxnda$^{2-}$ carboxylate oxygens are trans to one another, giving rise to the s-cis configuration, and the absolute configuration of the complex, assigned by the known absolute configuration of the $R,R$-chxn moiety as an internal reference, is Δ in agreement with the assignment made by analysis of the circular dichroism spectrum of the complex.[9] The tertiary nitrogen atoms are found to be both $S$. The $R,R$-chxn chelate takes the favored λ gauche conformation. The two N–CH$_2$ bonds of the acetate arms orient equatorially with respect to the central $R,R$-chxn chelate ring as originally predicted above.

The present crystal structure provides very important information to settle the structural question on (+)-*s-cis*-[Co($l$-sdda)(en)]$^+$ ($l$-sdda = (1$S$,2$S$)-1,2-diphenylethylenediamine) (**2**) prepared by Hawan, Mariconid, and Douglas.[14]

A positive dominant CD peak of **2** is observed in the first absorption region. They suggested the two possible structures for the complex: (1) (+)-[Co($l$-sdda)(en)]$^+$ has the Λ configuration based on the positive dominant CD sign. This assignment requires the large phenyl groups to occupy very unfavorable axial positions, contrary to the cases [Co($S,S$-stien)$_3$]$^{3+}$ [15] and [Pt(en)($S,S$-stien)]$^{2+}$ [16] ($S,S$-stien = (1$S$,2$S$)-1,2-diphenylethylenedimaine). (2) (+)-*s-cis*-[Co($l$-sdda)(en)]$^+$ has the Δ configuration based on the steric requirements of $S,S$-stien. It is consistent with the stable δ conformation of $S,S$-stien in [Co($S,S$-stien)$_3$]$^{3+}$ and [Pt(en)($S,S$-stien)]$^{2+}$. However, the observed CD sign is inverse to that for the Δ configuration. They concluded that the latter choice was preferred, but only an X-ray structure determination could settle the question with certainty.

However, both predictions are probably incorrect since these structural assignments were made on the assumption where the two N–CH$_2$ bonds of the acetate arms of the $l$-sdda$^{2-}$ would orient axially with respect to the central diamine chelate ring. When the N–CH$_2$ bonds of the acetate arms of the $l$-sdda$^{2-}$ orient equatorially as observed in the case of complex **1** and the $S,S$-stien backbone adopts the preferred δ conformation with both phenyl groups equatorial, the Λ absolute configuration of complex **2** could be easily expected as shown in Figure 1c. These structural assignments are quite consistent with the dominant CD peak of the complex (+)-*s-cis*-[Co($l$-sdda)(en)]$^+$.

Thus, the present crystal structure could establish the real existence of the novel isomer of *s-cis*-[Co(edda-type)(L)]$^n$ and related complexes containing the equatorially oriented N–CH$_2$ bonds of the terminal chelate rings.

**Registry No.** **1**, 93110-50-0.

**Supplementary Material Available:** Listings of positional and thermal parameters, mean square displacement tensors of atoms, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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(10) Crystal data: CoC$_{14}$H$_{28}$N$_4$O$_8$Cl, mol wt 474.72, wine red crystals (dimensions of the selected crystal 0.30 × 0.30 × 0.42 mm$^3$), monoclinic, space group $P2_1$, $a$ = 10.589 (4) Å, $b$ = 11.184 (4) Å, $c$ = 8.412 (3) Å, $\beta$ = 111.45 (3)°, $V$ = 927.210 Å$^3$, $D_{calcd}$ = 1.70 g cm$^{-3}$, $Z$ = 2, $\mu$(Mo K$\alpha$) = 11.48 cm$^{-1}$. Diffraction data ($2\theta < 65°$, $h_{max} = 14$, $h_{min} = 0$, $k_{max} = 15$, $k_{min} = -1$, $l_{max} = 11$, $l_{min} = -11$) were collected with Mo K$\alpha$ ($\lambda$ = 0.7107 Å) radiation monochromated by a graphite crystal. An absorption correction was applied. The structure was solved by conventional heavy-atom methods. A weighting scheme $1/w = \sigma c^2 + (0.015|F_o|)^2$ was employed, where $\sigma c$ defined as $\sigma c = (\bar{N})^{1/2}$ is a counting statistics error with Gaussian distribution function $P(N) = (1/2\bar{N})^{1/2} \exp[(N-\bar{N})^2/2\bar{N}]$. The source of the scattering factors was ref 11. The effects of anomalous dispersion were included in $F_c$, and values of $f'$ and $f''$ for Co, Cl, O, N, and C were taken from Cromer's tabulation.[12] Least-squares refinements converged at an $R$ value of 0.074 for 2418 independent reflections [$F_o > 5\sigma(F_o)$]. The calculations were carried out on the Hitachi M-200H computer at the Computer Center of this university with the Universal Crystallographic Computing System UNICSIII.[13]

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