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Synthesis and Structure of *trans*-Bis[[pentacarbonyl(*N*-(2-((diphenylphosphino)amino)ethyl)salicylaldiminato-*P*)]molybdenum(0)-*N*,*O*]copper(II): A Novel Trimetallic Complex with a Mixed P-Donor–Schiff-Base Bridging Ligand

Sir:

Polymetallic complexes that contain both hard and soft metal centers have recently received much attention for both their theoretical and their practical value.[1-7] The latter includes, in particular, the possibility that some of these complexes may exhibit enhanced catalytic activities relative to those of related monometallic complexes. Such enhancement of catalytic activity could result either directly, from interactions between the dissimilar metal centers,[6] or indirectly, from interactions of the heterometal centers with the substrate.[7] The freedom of movement of the hard and soft metal centers with respect to one another likely affects the degree of interaction between these centers, which might, in turn, influence catalytic interactions between metal and substrate. However, a common feature of the heteropolymetallic complexes that have been studied thus far is the constrained arrangement in which the metal atoms are held by two or more multidentate ligands. We have, therefore, undertaken a series of synthetic and crystallographic studies of polymetallic complexes in which hard and soft metals are bridged by only a single multidentate ligand. We report here the synthesis and the molecular structure of the trinuclear complex *trans*-$[(CO)_5Mo(Ph_2PNHCH_2CH_2N{=}CHC_6H_4\text{-}o\text{-}O)]_2Cu$ (I).

The reaction scheme employed in the synthesis of I is outlined in Figure 1 and is similar to that previously reported for the synthesis of *trans*-[*cis*-$(CO)_4Mo(PPh_2NHCH_2CH_2N{=}CHC_6H_4\text{-}o\text{-}O)_2]Ni$ (II).[1] This method offers several advantages over those that have been used for the syntheses of other heteropolymetallic complexes.[2-7] Coordination of the chlorodiphenylphosphine ligands to the molybdenum atoms prior to formation of the heterometal coordination site provides a high degree of control over the coordination environments of each of the metal centers. Prior coordination of chlorodiphenylphosphine to the molybdenum also markedly reduces both the oxygen and the water sensitivities of the P-donor group. This, together with the fact that the complexes are solids, greatly simplifies handling and purification of the materials. Finally, and perhaps most importantly, this method can be used to synthesize a variety of heteropolynuclear complexes simply by varying the type of chlorophosphine complex used.

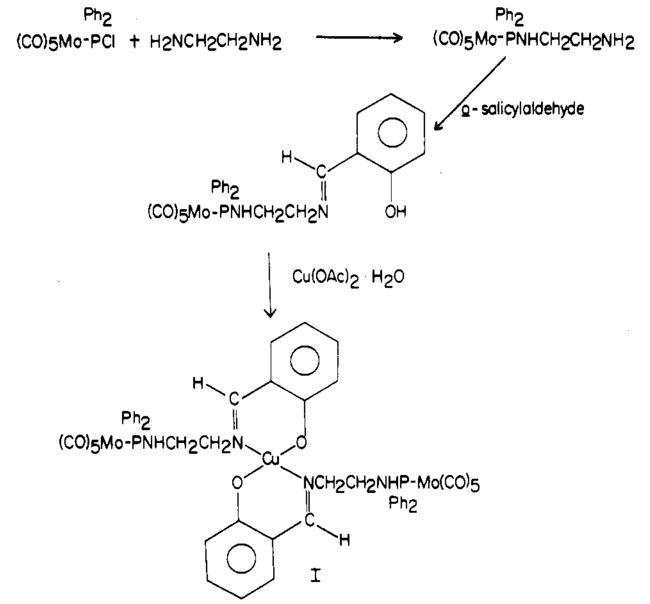

Figure 1. Synthetic scheme for *trans*-$[(CO)_5Mo(Ph_2PNHCH_2CH_2N{=}CHC_6H_4\text{-}o\text{-}O)]_2Cu$ (I).

Dark brown, prismatic crystals of the THF solvate of I were obtained from THF/ethyl ether by rapid cooling. The crystals are triclinic, space group $P\bar{1}$, and contain two molecules of I and four THF molecules per unit cell.[8] The Cu(II) ions of the two independent molecules occupy inversion centers at 0, 0, 0 and $^1/_2$, $^1/_2$, 0. The molecules at 0, 0, 0 and at $^1/_2$, $^1/_2$, 0 are designated A and B, respectively, and are depicted in Figure 2. The molecules differ primarily in their conformation about the Mo–P bond, as described by the C(3)–Mo–P–N torsional angles of 70.7 (1) and 158.4 (1)° for molecules A and B, respectively.

The molecular centrosymmetry necessitates an essentially trans square-planar arrangement of the salicylaldiminato-*N*,*O* ligands about the Cu(II) ions (∠O–Cu–N = 91.60 (6) and 91.77 (6)° in molecules A and B, respectively). This ligand arrangement results in distances of only 2.786 (3) and 2.787 (3) Å between atoms O(6) and C(9) within molecules A and B of I, respectively. The nontetrahedrally distorted square-planar configuration was unexpected, as other *trans*-bis(salicylaldiminato-*N*,*O*)copper(II) complexes with bulky N substituents show considerable tetrahedral distortion from a square-planar configuration.[9,10] The arrangement of the salicylaldiminato ligands around the Ni in the analogous doubly bridged complex II is also tetrahedrally distorted from a square-planar configuration.

The nontetrahedrally distorted square-planar coordination of the Cu(II) in I may be due to intramolecular stacking interactions

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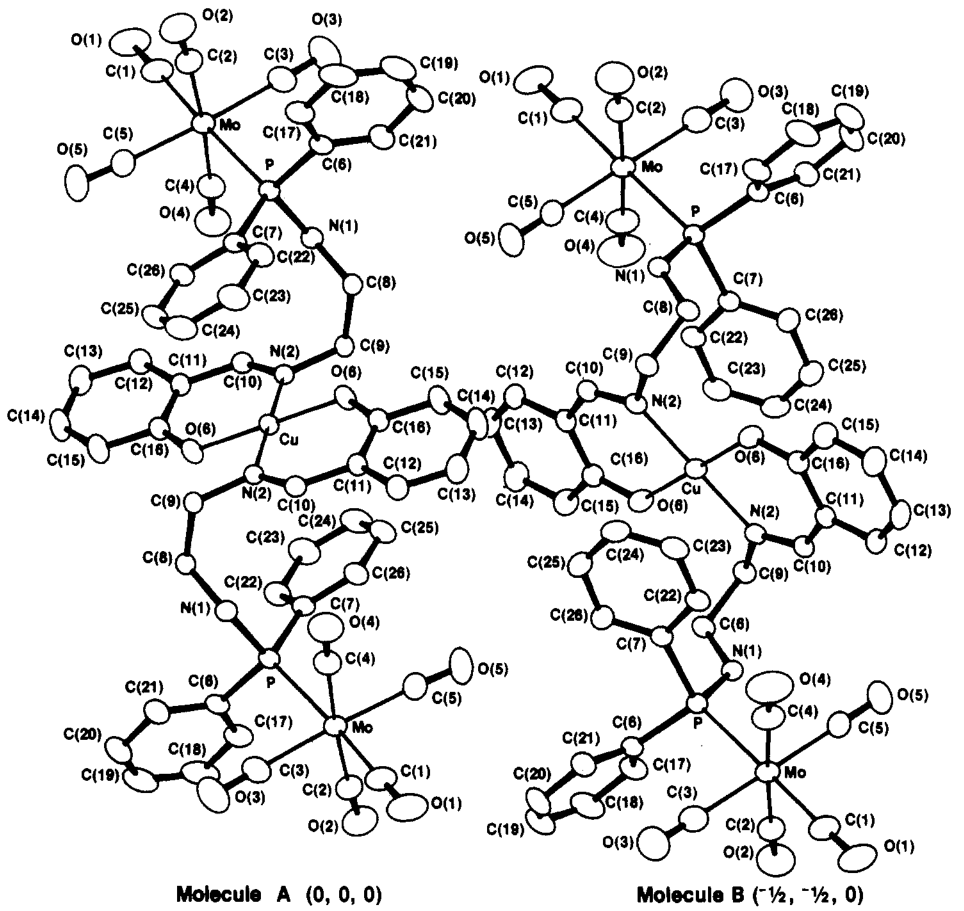

Figure 2. Structures of the two independent molecules of I, designated A (0, 0, 0) and B ($-^1/_2$, $-^1/_2$, 0), as related in the unit cell.[13] Atoms are represented by thermal ellipsoids drawn at the 25% probability level. The hydrogen atoms have been omitted for clarity.

between one of the polarizable phenyl rings of each phosphinoamino group and the polar atoms of the *trans*-bis(salicylaldiminato-*N*,*O*)copper(II) group. The plane through atoms N(2), C(10), C(11), C(16), O(6), and Cu of the salicylaldiminato–Cu chelate is nearly parallel to the plane through atoms C(7), C(22), C(23), C(24), C(25), and C(26) of a phenyl group in both molecules A and B (dihedral angles are 14.4 (1) and 14.5 (1)°, respectively). The spacings between these planes in molecules A and B are 3.15 (1) and 3.14 (1) Å, respectively. The closest contacts between atoms in these planes, in molecules A and B, are made respectively by atoms O(6) and C(25) at 3.406 (3) and 3.414 (3) Å, by the Cu(II) ion and atom C(24) at 3.557 (3) and 3.549 (3) Å, by the Cu(II) ion and atom C(25) at 3.530 (3) and 3.507 (3) Å, and by atoms N(2) and C(26) at 3.547 (3) and 3.532 (3) Å. These types of interactions are common in crystals of aromatic compounds containing heteroatoms or polar substituents and those of aromatic charge-transfer complexes and are apparently controlled by dipole-induced dipole forces that involve a partial bond moment and a polarizible π-electron system.[11]

The interaction between the phenyl ring of the phosphinoamino groups and the *trans*-bis(salicylaldiminato-*N*,*O*)copper(II) group may also be occurring in solution. Multinuclear NMR studies of the Ni(II) analogue of compound I indicate that the compound is diamagnetic in solution. This would only occur if the Ni(II) ion occupies a non tetrahedrally distorted square-planar coordination site. The results of these studies will be presented in a later communication.

The arrangements of the ligands about the molybdenum atoms

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(8) A prismatic crystal (0.4 mm × 0.3 mm × 0.2 mm) was used for structure determination. $a = 11.317$ (1) Å, $b = 15.032$ (1) Å, $c = 18.752$ (1) Å, $\alpha = 95.613$ (6)°, $\beta = 97.984$ (6)°, and $\gamma = 90.22$ (1)°, as determined by a least-squares analysis of the diffractometer setting angles for 12 medium-resolution reflections (Cu Kα = 1.5418 Å, T = 21 °C). Intensities (I) were measured (20 °C ≤ T ≤ 22 °C) for all 10 438 unique reflections with 2° ≤ 2θ ≤ 128° ($+h,\pm k,\pm l$) by use of Ni-filtered Cu radiation and an automated Picker FACS-1 four-circle diffractometer. Of these reflections 10 039 had $|F| > 0$. Three reflections that were remeasured periodically during data collection to monitor crystal decay showed no significant fluctuations. Variances were assigned to I's on the basis of counting statistics, with addition of an instrumental uncertainty term, $(0.03S)^2$, S being the scan count. Lorentz, polarization, and analytical absorption corrections (minimum and maximum transmission factors 0.29 and 0.40) were made to I and σ^2 values with use of the ABSCOR program of the Enraf-Nonius SDP series of programs. The absorption coefficient u was calculated to be 48.044. Scattering factors were obtained from: Cromer, D. T.,; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1. A suitable trial structure was obtained by conventional Patterson and Fourier methods and refined by a full-matrix least-squares analysis that minimized $w(|F_o| - k|F_c|)^2$, where $w = 1/\sigma^2(F_o)$.[13] Final cycles of refinement varied k, positional and anisotropic thermal parameters for the non-H atoms, and an isotropic secondary extinction parameter and included fixed contributions from the H atoms. At convergence (maximum shift esd = 0.06), the R value $(\sum||F_o| - k|F_c||/\sum|F_o|)$ is 0.045 and the goodness of fit $([\sum w(|F_o| - k|F_c|)^2/v]^{1/2}$, where v = number of observations minus number of variables) is 1.96, considering all 10 438 data. Except for a trough of −0.71 e Å^{-3} in the vicinity of the Mo atom in molecule B, extrema of the final difference Fourier map did not exceed 0.52 e Å^{-3} in magnitude. Tables of atomic parameters are available as supplementary material.

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in the two independent molecules of I are best described as slightly distorted octahedra similar to those found in other $(CO)_5Mo$(P-donor ligand) complexes.[12] The dihedral angles formed by the three equatorial planes of four donor atoms are 90.1 (1), 87.4 (1), and 89.8 (1)° in molecule A and 87.6 (1), 90.2 (1), and 89.3 (1)° in molecule B. As previously observed in other complexes of the type $(CO)_5M$(P-donor ligand) and $(CO)_4M$(P-donor ligand)$_2$ (M = Cr, Mo),[1,12] the lengths of the Mo–C bonds involving the CO ligands trans to the P-donor groups (1.998 (3) and 2.003 (3) Å in A and B, respectively) are significantly shorter than the average of those involving CO ligands cis to the P-donor groups (2.040 (3) and 2.038 (3) Å in molecules A and B, respectively).

The Mo(0) atom and the Cu(II) ion in I are separated by distances of 7.078 (1) and 7.079 (1) Å in molecules A and B. These distances are considerably longer than the 5.679 (1) Å Mo–Ni distance in II[1] and the 3.966 (1) Å Pt–Cu distance in *cis*-$Cl_2Pt(Pacac)_2Cu$ (III; PacacH = [*o*-(diphenylphosphino)-benzoyl]pinacolone).[4] The differences in the metal–metal distances in these complexes is due to both (i) differences in the flexibility and the size of the bridging ligand (II vs. III) and (ii) differences in the degree of restraint on relative metal positions due to differences in the number of bridging ligands (I vs. II).

The structure of the title compound, in comparison with those of other heteropolymetallic complexes, suggests several features that appear to be related to the presence of a single salicylaldiminato–diphenylphosphino bridging ligand between the metal centers. These include (i) the stacking interactions between a phenyl ring of the phosphino ligand group and the polar or partially charged atoms at the heterometal center and (ii) the expansion of the distance separating the metal centers relative to that in the related heterobimetallic complex II, in which the centers are bridged through two salicylaldiminato–diphenylphosphino ligands. These features may be of significance to the catalytic properties of complexes similar to I and II, in which the molybdenum center is replaced by catalytically active group 9 or 10 metals. The syntheses and structural analyses of complexes of the latter type are currently in progress.

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Registry No. I, 102942-28-9; $(CO)_5MoPPh_2NHCH_2CH_2NH_2$, 102942-29-0; $(CO)_5MoPPh_2NHCH_2CH_2N{=}CH$-*o*-$C_6H_4OH$, 102942-30-3; $(CO)_5MoPPh_2Cl$, 23581-74-0; $PPh_2NHCH_2CH_2NH_2$, 102942-27-8; *o*-salicylaldehyde, 90-02-8.

Supplementary Material Available: A listing of atomic positional and thermal parameters (6 pages). Ordering information is given on any current masthead page.

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Articles

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Magnetic Circular Dichroism Spectra for the Tetraammineplatinum(II) and Bis(ethylenediamine)platinum(II) Cations

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Electronic absorption and magnetic circular dichroism (MCD) spectra are reported for $[Pt(NH_3)_4](ClO_4)_2$ and for $[Pt(en)_2](ClO_4)_2$ (en = ethylenediamine) in 0.100 M $HClO_4$ and in CH_3CN in the UV region from 2.8 to 5.2 μm^{-1}. The spectra for the two cations are remarkably similar. A weak feature, which has no counterpart in the absorption, is observed near 3.1 μm^{-1} in the MCD spectra for both cations. This feature, which has not been reported previously, and two other bands in the 3.0–4.3-μm^{-1} region are ascribed to ligand field (LF) transitions. A strong MCD minimum associated with the more intense absorption band near 4.5 μm^{-1} is shown by moment analysis to consist of a significant positive $\mathcal{A}$ term and a negative $\mathcal{B}$ term. The intense band in the region 4.9–5.1 μm^{-1} observed for both cations shows a strong positive $\mathcal{A}$ term in the MCD. In addition, a negative $\mathcal{B}$ term is resolved on the low-energy side of the strong positive $\mathcal{A}$ term for this band for $Pt(NH_3)_4^{2+}$ in 0.100 M $HClO_4$. Both the band near 4.5 μm^{-1} and the intense band at 4.9–5.1 μm^{-1} are interpreted in terms of dipole-allowed 5d → $6p_z$ transitions. This interpretation leads to new assignments of these bands and an ordering of the occupied 5d MO's of $a_{1g}(z^2) > b_{2g}(xy) \simeq e_g(xy,yz)$. This ordering is discussed in the context of its similarity to that of $Pt(CN)_4^{2-}$.

Introduction

The electronic absorption spectrum of the D_{4h} square-planar $Pt(NH_3)_4^{2+}$ cation in aqueous solution consists of a weak broad band at 3.5 μm^{-1} (ϵ 44), a shoulder near 4.2 μm^{-1} (ϵ 155), and another shoulder near 4.5 μm^{-1} (ϵ 480).[1-4] These three bands have been assigned as ligand field (LF) transitions on the basis of their low intensities.[1,2] The temperature dependence of the first two bands in single crystals of $[Pt(NH_3)_4]SO_4$ has shown that they are vibronic and thus consistent with the LF assignment.[3]

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