obtained after stripping the solvent were analyzed by mass spectroscopy. MoW-containing ions were present, in particular $Cp_2MoW(CO)_4^+$ and Cp_2MoW^+. The relative intensities of Mo_2^+-, MoW^+-, and W_2^+-containing ions were ca. 1:2:1.

(c) At 120 °C, 12 h. $Cp_2Mo_2(CO)_4$ and $Cp_2W_2(CO)_4$ were dissolved in *m*-xylene (20 mL) as in (a) above. The solution was heated in an oil bath and maintained at ca. 120 °C (reflux) for 24 h. The solid obtained after stripping the solvent was analyzed by mass spectroscopy. The mass spectrum was virtually identical with that obtained in (b) above.

$Mo_2(NMe_2)_6$ + $W_2(NMe_2)_6$; $W_2(NMe_2)_6$ + $W_2(NMe_2)_6$-d_{36}. Equimolar quantities of the appropriate dimethylamides were dissolved in toluene as above and either heated to 80 °C in an oil bath or maintained at ca. room temperature and exposed to UV irradiation for 12 h. The solids obtained after stripping the solvent were analyzed by mass spectroscopy. The spectra corresponded to a superimposition of the spectra obtained for $Mo_2(NMe_2)_6$ and $W_2(NMe_2)_6$. No MoW-containing ions were observed.

$Mo_2(CH_2SiMe_3)_6$ + $W_2(CH_2SiMe_3)_6$. Equimolar quantities of $Mo_2(CH_2SiMe_3)_6$ and $W_2(CH_2SiMe_3)_6$ were dissolved in toluene and reacted thermally and photochemically as above. No MoW-containing ions were detected in the mass spectrum of the resulting solids.

Preparation of the Tungsten–Molybdenum Chloride of Empirical Formula "MoW_2Cl_{12}". WCl_6 (28.03 g, 70.68 mmol) was added to $Mo(CO)_6$ (9.33 g, 35.34 mmol) in a 500-mL flask. A reaction appeared to take place between the two solids and on addition of chlorobenzene (50 mL) a vigorous, but smooth, reaction occurred with gas evolution. After 12 h, a brown solid had formed and the reaction mixture was then refluxed for a further 3 h. Removal of solvent gave 29.15 g of a black solid (92.8% yield based on "MoW_2Cl_{12}"), which did not show any evidence of residual CO ligands in the infrared spectrum. The product was used without further purification and is assigned the empirical formula "MoW_2Cl_{12}" based on the following analytical data. Anal. Calcd: Mo, 10.79; W, 41.36; Cl, 47.85. Found: Mo, 10.91; W, 41.09; Cl, 46.58.

Reaction of "MoW_2Cl_{12}" with $LiNMe_2$. $LiNMe_2$ was generated by the addition of $HNMe_2$(142.1 mmol) to BuLi (142.1 mmol) in hexane (62 mL) at −80 °C. The reaction mixture was allowed to warm to room temperature and then diethyl ether (100 mL) was added to give a slurry of white $LiNMe_2$. The slurry was then cooled to 0 °C and "MoW_2Cl_{12}" (10.53 g, 11.84 mmol) added over a period of 30 min, after which time the reaction was allowed to warm to room temperature. After stirring for 24 h, the yellow-brown solution was filtered from the gray precipitate of lithium chloride and the solvent removed under vacuum. The residue was then dissolved in boiling hexane (100 mL) and filtered and the solvent removed from the filtrate to give a dark brown solid.

Vacuum sublimation (10^{-2} mmHg) of the brown residue gave a trace of the purple compound $Mo(NMe_2)_4$ at 50 °C, and at 100–120 °C an orange solid sublimed (1.18 g). The mass spectrum of the orange solid showed in addition to ions derived from $Mo_2(NMe_2)_6$ and $W_2(NMe_2)_6$, several ions attributable to MoW-containing species, most notably $MoW(NMe_2)_6^+$.

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Registry No. $Cp_2Mo_2(CO)_4$, 56200-27-2; $Cp_2W_2(CO)_4$, 62853-03-6; $Mo_2(NMe_2)_6$, 51956-20-8; $W_2(NMe_2)_6$, 54935-70-5; $W_2(NMe_2)_6$-d_{36}, 60475-04-9; $Mo_2(CH_2SiMe_3)_6$, 34439-17-3; $W_2(CH_2SiMe_3)_6$, 36643-37-5; WCl_6, 13283-01-7; $Mo(CO)_6$, 13939-06-5; $LiNMe_2$, 3585-33-9; $Cp_2MoW(CO)_4$, 65995-85-9; MoW_2Cl_{12}, 66102-07-6; $MoW(NMe_2)_6$, 65995-84-8.

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Contribution from the Department of Chemistry and Geology,
Clemson University, Clemson, South Carolina 29631

Bidentate Chelate Compounds. 2. Peroxobis(2,2′-bipyridylamine)cobalt(III) Perchlorate: a Novel Monomeric Cobalt(III) Peroxide Complex[1]

W. Leo Johnson III and John F. Geldard*

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The ability of 2,2′-bipyridylamine (HL) to coordinate to transition-metal ions has been extensively investigated.[2–4] A diversity of metal ions has been used (nickel(II),[5] cobalt(II),[3] iron(II),[6] copper(II),[7] palladium(II),[8] rhodium(III), iridium(III)[9]) and studied by various techniques (x-ray structures,[10–12] ESR and single-crystal polarized spectra,[13] Mössbauer spectra,[14] far-IR spectra[15]). To date, however, no cobalt(III) complexes of this ligand have been reported.

In conjunction with our interest in the circular dichroism of chiral molecules of various symmetries, we undertook the preparation and resolution of the tris(2,2′-bipyridylamine)cobalt(III) ion, $Co(HL)_3^{3+}$. It has been reported[3] that the obvious precursor, $Co(HL)_3^{2+}$ ion, is degraded by good competing ligands, such as halide ions, and that its attempted oxidation with any of H_2O_2, Cl_2, Br_2, $Pb(OAc)_4$, or $KMnO_4$ does not yield $Co(HL)_3^{3+}$ ion.[16]

We now report that the oxidation of $Co(HL)_3^{2+}$ ion with H_2O_2 does indeed degrade the ion, but with the formation of the title compound, apparently a unique monomeric peroxocobalt(III) complex.

Experimental Section

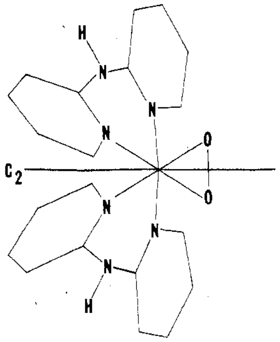
All analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. Diffuse-reflectance spectra were measured with a Cary 14 recording spectrophotometer, modified with a Varian Model 1411 diffuse-reflectance accessory. Infrared spectra were measured with Perkin-Elmer 137 Infracord and 621 spectrophotometers. A Faraday balance was used to determine the magnetic moments of the complexes. The reagents $Co(ClO_4)_2{\cdot}6H_2O$ and $NaClO_4{\cdot}H_2O$ were obtained from the G. Frederick Smith Co.; reagent grade H_2O_2 (30%) was obtained from Fisher Scientific Co. The ligand 2,2′-bipyridylamine (Aldrich Chemical Co.) was recrystallized from ethanol before use.

Preparation of $Co(HL)_2O_2ClO_4$ Orange $Co(HL)_3(ClO_4)_2$ (3.00 g, 0.00389 mol; prepared by the method of Goodgame[3]) was oxidized by mixing with H_2O_2 (30%, 20 mL), resulting in a red solution. The mixture was heated at 60 °C for 30 min, and then $NaClO_4{\cdot}H_2O$ (2.00 g, 0.014 mol) was added. On cooling, 2,2′-bipyridylamine and $Co(HL)_2O_2ClO_4$ cocrystallized. The mass of crystals was collected on a medium-porosity glass filter and was washed with 100 mL of distilled water in 20-mL portions. The mixture was flushed into a 250-mL Erlenmeyer flask with 100 mL of absolute ethanol and allowed to stand for 30 min with stirring. After this extraction procedure, the dark red crystals were collected on a medium-porosity glass filter, washed with 60 mL of absolute ethanol, and allowed to air-dry. The yield of the diamagnetic ($\mu_{eff} = 0$) salt was 1.57 g (75.9% yield). Anal. Calcd for $CoC_{20}H_{18}N_6ClO_6$: Co, 11.18; C, 45.08; H, 3.41; N, 15.78; Cl, 6.65. Found: Co, 10.99; C, 44.92; H, 3.53; N, 15.62; Cl, 6.82.

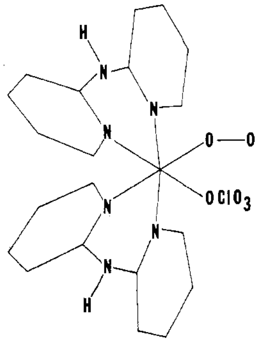
Results and Discussion

Elemental analysis establishes the empirical formula $Co(HL)_2O_2ClO_4$. The cobalt(III) oxidation state is indicated by the diamagnetism of the compound and the presence of the peroxo group by the moderately intense absorption at 892 cm^{-1}. The presence of N–H bending modes at 1645 cm^{-1} and of weak N–H stretches at 3290 cm^{-1} indicates that the ligands are not deprotonated. There are no water or hydroxide modes present in the spectrum. Thus, the alternative formulations $[Co(HL)_2(OH)_2]ClO_4$ and $[Co(L)_2(H_2O)_2]ClO_4$ are eliminated. These differ from the formulation assigned to the complex by only two hydrogen atoms and have essentially the same percentage composition.

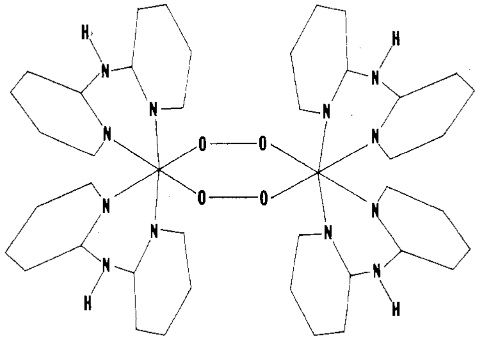
We assign this complex the structure I rather than the structure II, in which the perchlorate ion also acts as a ligand. In structures I, II, and III, the bidentate ligand is represented by its C and N skeleton; the structure of the ligand HL is shown below. The perchlorate ion absorbs at 1060, 1100, and 1115 cm^{-1}. This is taken to indicate that the site symmetry of the perchlorate ion in the crystal is less than T_d rather than that the ion is coordinated to the cobalt. In the closely related compound $[Co(HL)_2CO_3]ClO_4$,[16] in which the carbonato group is unambiguously bidentate, the uncoordinated perchlorate ion shows similar nondegenerate absorptions at 1073, 1098, and 1117 cm^{-1}.



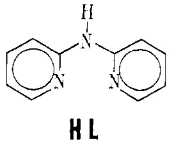
I



II



III



HL

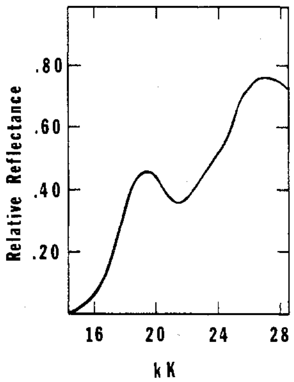


Figure 1. Electronic spectrum of $Co(HL)_2O_2ClO_4$.

Structure I is also preferred to structure II because end-on-bonded peroxides absorb generally near 1134 cm^{-1} whereas bidentate peroxides absorb generally near 880 cm^{-1}.[17]

In addition to the intense ν_{CoO_2} band, the IR spectrum of I exhibits absorptions at 565, 542, and 535 cm^{-1} that have been assigned to an undetermined metal–peroxo vibrational mode.[18]

Dimeric structures for the complex, such as III, can be ruled out because it has been established that the peroxide groups in bridged peroxo complexes do not absorb in the IR.[19-21]

Thus, on the basis of the available evidence, it is concluded that this peroxocobalt(III) complex has structure I.

The complex is extremely insoluble in such solvents as water, ethanol, chloroform, benzene, DMF, Me_2SO, or monoglyme. It can be made to dissolve in water and ethanol by the use of chloride ion exchange resins, but its rapid decomposition ensues, the decomposition being accelerated by heat or the addition of acid.[22] The diffuse-reflectance spectrum of the complex (Figure 1) is very similar to that of the carbonato complex, and the fact that both are diamagnetic red complexes with the components of the $^1T_{1g}$ manifold maximizing at 19×10^3 cm^{-1} indicates that they have very similar coordination spheres.

This peroxo complex is unique in that it is the first reported peroxo complex of cobalt(III) that is monomeric and yet contains simple nitrogen donor ligands. Of the monomeric peroxo complexes with reported crystal structures,[23-25] the most closely related one is dioxygenbis(*cis*-1,2-bis(diphenylphosphino)ethylene)cobalt tetrafluoroborate.[23] This complex, which is generally considered to be a dioxygen complex of cobalt(I) rather than a peroxo complex of cobalt(III), has a virtual C_2 axis as does I and also has the characteristic absorption at 909 cm^{-1} in chloroform solution. The presence of these moderately intense bands in these two complexes requires comment.

These two complexes have approximately C_2 symmetry. In this point group, the O–O stretching mode transforms as the totally symmetric representation A; thus, only the z component of the transition dipole moment integral may be nonzero, a direction to which the mode itself is orthogonal. For small displacements, the mode produces no dipole moment change. Thus, to first order, the transition probability is zero.[26]

In order to explain the intensity of the observed transition and to rationalize it in terms of an interaction with the z component of the impinging radiation, this mode must be considered to have a considerable contribution to it from the totally symmetric Co–O stretching mode and the O–Co–O bond angle deformation or a ring deformation mode. Such a mode would produce a significant dipole moment change along the molecular axis and probably corresponds to the $\nu_3(A)$ vibration observed at 771 cm^{-1} in the bidentate carbonato complexes of cobalt(III).[27]

In any event, the observed transition is not satisfactorily explained in terms of a simple O–O stretching mode.

Registry No. $Co(HL)_2O_2ClO_4$, 65956-93-6; $Co(HL)_3(ClO_4)_2$, 15412-27-8.

Supplementary Material Available: A figure showing the IR spectrum of $Co(HL)_2O_2ClO_4$ as a Nujol mull (1 page). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Massachusetts, Amherst, Massachusetts 01003

Preparation of Tetrakis(picolinato)molybdenum(IV)

Craig J. Donahue and Ronald D. Archer*

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The oxidative decarbonylation of tungsten hexacarbonyl by picolinic acid, 2-pyridinecarboxylic acid, to yield tetrakis(picolinato)tungsten(IV), $W(pic)_4$, has recently been reported by us[1] and also by Dorsett and Walton.[2] We have successfully extended this reaction to produce the eight-coordinate complex tetrakis(picolinato)molybdenum(IV). A previous study[2] reports the oxidation of molybdenum hexacarbonyl by picolinic acid to yield exclusively $Mo(pic)_3$ under milder reaction conditions. The successful synthesis of $Mo(pic)_4$ is apparently dependent on the reaction conditions employed, whereas the synthesis of $W(pic)_4$ can be carried out over a much more diverse range of reaction conditions. The $Mo(pic)_4$ complex has been characterized and its chemistry is compared to that of the $W(pic)_4$ complex and other early transition metal eight-coordinate complexes.

Experimental Section

Synthesis of Tetrakis(picolinato)molybdenum(IV). Molybdenum hexacarbonyl (Pressure Chemical) was purified by vacuum sublimation at 100 °C and stored over potassium hydroxide prior to use. Mesitylene (Eastman) and picolinic acid (Eastman) were used without further purification.

(a) Picolinic acid (3.70 g, 30.0 mmol) and molybdenum hexacarbonyl (0.79 g, 3.00 mmol) were placed in a long-necked 50-mL round-bottom flask with a magnetic stirrer bar. After purging the system with prepurified nitrogen, the flask was immersed in an oil bath at 150 °C. The formation of a dark brown solution began concurrently with the melting of the picolinic acid. No further color changes were observed. The crude product was subjected to vacuum sublimation at 150 °C for 4 h. This treatment removed most of the unreacted $Mo(CO)_6$ and picolinic acid. The complex was then dissolved in methylene chloride, the solution filtered, and hexane added to the filtrate to cause precipitation of $Mo(pic)_4$. The complex was dried in vacuo over potassium hydroxide for 24 h.

Anal. Calcd for $Mo(C_6H_4NO_2)_4$: C, 49.23; H, 2.76; N, 9.59. Found: C, 49.01; H, 3.21; N, 9.06. Yield $\geq$70%.

(b) Picolinic acid and molybdenum hexacarbonyl (in a 5:1 mole ratio) were allowed to react in mesitylene under reflux conditions and a nitrogen atmosphere for 4 h. After flash evaporation of the solvent, the workup of the complex was identical with (a). Yield $\geq$70%.

Characterization of Tetrakis(picolinato)molybdenum(IV). (1) Electronic Spectrum. The electronic spectrum of the complex was recorded from 10 000 to 40 000 cm^{-1} on a Hatachi Model EPS-3T spectrophotometer at room temperature. Matched Suprasil cells of 1.000-cm path length were employed in the double-beam measurements. The reference cell contained the same solvent as the sample solution.

(2) Magnetic Susceptibility Measurements. The Faraday method was used for determining the magnetic susceptibility of the complex. $CoHg(SCN)_4$ was used to calibrate the balance. Sample size was ca. 5 mg. The diamagnetism of the ligand was corrected for using Pascal's constant summation method.

(3) Proton Nuclear Magnetic Resonance Spectrum. The ^1H NMR spectrum of the complex was measured on a 90-MHz Perkin-Elmer R32 nuclear magnetic resonance spectrometer. The spectrum was referenced against tetramethylsilane. The reported temperature is accurate to ±2 °C.

(4) Infrared Spectrum. The infrared spectrum was recorded on the Perkin-Elmer 180 spectrometer. The sample was run as a KBr disk vs. air.

Results and Discussion

Whereas Dorsett and Walton[2] report that the reaction of $Mo(CO)_6$ and picolinic acid (1:4 mole ratio) in refluxing methanol or acetonitrile yields only the tris(picolinato)molybdenum(III) complex, we have obtained $Mo(pic)_4$ in high yields, by running the reaction at a higher temperature and by increasing the ligand to $Mo(CO)_6$ mole ratio. The $Mo(pic)_3$ complex is paramagnetic, $\mu_{eff} = 3.74\ \mu_B$, and is susceptible to rapid oxidation in air.[2] The diamagnetic $Mo(pic)_4$ complex ($\chi_g = -0.15 \times 10^{-6}$ cgsu, $\chi_m = -90 \times 10^{-6}$, $\chi_m{}^{cor} = 150 \times 10^6$ at 23 °C) has a $\mu_{eff} = 0.6\ \mu_B$ (zero within experimental error). The slight paramagnetism of the complex may be due to temperature-independent paramagnetism and/or trace amounts of paramagnetic impurities.

While the purple $W(pic)_4$ complex persists in aqueous solution for months,[1] the $Mo(pic)_4$ complex is hydrolyzed within a day. The infrared spectrum of $Mo(pic)_4$, like $W(pic)_4$, is dominated by the $\nu(COO)_{as}$ band at 1674 cm^{-1}. In addition, the spectrum is free of any bands logically assignable to Mo–CO, Mo–O, or Mo–OH units.

The visible spectrum of $Mo(pic)_4$ in $CHCl_3$ is dominated by moderately intense absorption bands at 20 500 cm^{-1} (ϵ 5500) and a weaker band at 27 800 cm^{-1} (ϵ 2000). A maxima at 37 900 cm^{-1} (ϵ 16 000) and a shoulder at 36 500 cm^{-1} (ϵ 13 000) are assigned as $\pi \rightarrow \pi^*$ transitions of the ligand. The low-energy transition of the $Mo(pic)_4$ complex can be assigned as

0020-1669/78/1317-1677$01.00/0