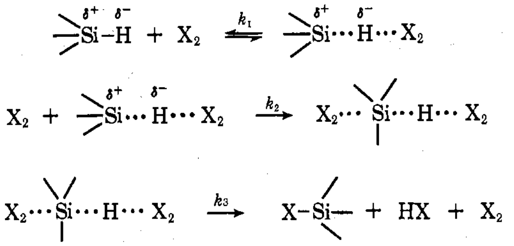
Discussion

The spectral and physical property data shown above allow for the complete characterization of the $BrSi_3H_7$ isomers. The ^1H nmr spectra for both 1- and 2-$BrSi_3H_7$ are consistent with the proposed structures. The peaks at 2160 and 2170 cm^{-1} in the infrared spectra of 2-$BrSi_3H_7$ and 1-$BrSi_3H_7$, respectively, are characteristic of the Si–H stretching absorption.[17] Due to the complexity of the spectra, further assignments were not attempted. The mass spectra of both 1- and 2-$BrSi_3H_7$ exhibit fragmentation patterns of the type expected for bromotrisilanes. The mass spectra for both compounds consist of envelopes at (assignments in parentheses) m/e 176–163 ($BrSi_3H_x^+$), 144–135 ($BrSi_2H_x^+$), 112–107 ($BrSiH_x^+$), 96–84 ($Si_3H_x^+$), 63–56 ($Si_2H_x^+$), and 33–28 (SiH_x^+). A strong molecular ion envelope was observed for both isomers. The two most intense peaks in the mass spectrum of 2-$BrSi_3H_7$ occur at m/e 138 and 140, corresponding to the loss of a neutral SiH_4 from the molecular ions $^{79}Br^{28}Si_3H_7^+$ and $^{81}Br^{28}Si_3H_7^+$. The most intense peak in the spectrum of 1-$BrSi_3H_7$ occurs at m/e 60, corresponding to the loss of a neutral $BrSiH_3$ from the molecular ion $Br^{28}Si_3H_7^+$. This fragmentation is consistent with the proposed structural assignment of the isomers and with the observed fragmentation of trisilane.[12] The most intense peak in the mass spectrum of trisilane occurs at m/e 60 resulting from the loss of a neutral SiH_4 from the molecular ion $^{28}Si_3H_7^+$.

The isomers of $CH_3Si_2H_4Br$ were also prepared in this study; however, since we were interested only in isomer distribution of the monobromo products, they were not separated for complete characterization. The ^1H nmr spectra of the mixture provides clear evidence for the presence of both the 1 and 2 isomers. As shown by the spectrum in Figure 3, the 1-Br-1-$CH_3Si_2H_4$ isomer predominates in the product mixtures.

The mechanisms of the silane bromination reactions appear analogous to those proposed for the bromination[25] and iodination[26] of trisubstituted silane. In these cases, the kinetics of the halogenation reactions were consistent with electrophilic attack on H by the halogen



where $k_1 < k_3 \ll k_2$. Electron-donating groups on silicon were found to enhance the rate of substitution. Thus, for disilane, substitution of one hydrogen by a bromine should decrease the rate of further bromination and direct the second bromine atom to the adjacent silicon atom. Analysis of the polybromodisilanes formed in our studies indicate the predominance of 1,2-$Br_2Si_2H_4$ over 1,1-$Br_2Si_2H_4$. Substitution of electron-donating groups CH_3[27,28] and SiH_3[29] for H on Si_2H_6 should enhance the rate of bromination of the substituted silicon; thus, we observe the predominance of 2-$BrSi_3H_7$ over 1-$BrSi_3H_7$ and 1-Br-1-$CH_3Si_2H_4$ over 2-Br-1-$CH_3Si_2H_4$ in the brominations of Si_3H_8 and $CH_3Si_2H_5$, respectively.

Acknowledgment.—This work was supported by National Science Foundation Grant GP-8090.

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[25] G. Schott and H. Werner, *Z. Anorg. Allg. Chem.*, **329**, 229 (1964).

[26] D. R. Deans and C. Eaborn, *J. Chem. Soc.*, 3169 (1954).

[27] F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112 (1955).

[28] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960.

[29] S. D. Gokhale and W. Jolly, *Inorg. Chem.*, **3**, 946 (1964).

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Preparation and Characterization of μ-Superoxo-bis[bis(L-histidinato)cobalt(III)] Salts[1]

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Received September 22, 1971

In a previous note,[3] preparation and electron paramagnetic resonance studies in solution of a previously unknown μ-superoxo-bis[bis(L-histidinato)cobalt(III)] complex were reported. Herein, we describe the preparation of salts of this ion and summarize our findings as to its molecular weight, charge, and unpaired electron content.

Experimental Section

Preparation of μ-Superoxo-bis[bis(L-histidinato)cobalt(III)] Trinitrate.—As a starting material, μ-peroxo-bis[bis(L-histidinato)cobalt(III)] was prepared,[4] and about 5 g was slowly added to 10 ml of 15 *M* HNO_3, with stirring on a cold plate at *ca.* −10°. The temperature was not allowed to exceed 0°. During the addition, the color changed to dark green. The solution was diluted to 200 ml and poured onto a 40-cm ion-exchange column containing *ca.* 650 cm^3 of Dowex 50-X-2 resin. The column was washed with successive additions of 1 *M* HNO_3 (which produced a pale pink eluent, presumably Co^{2+}) and then 2 *M* HNO_3, and finally the dark green band was removed with 3 *M* HNO_3. This green fraction was evaporated under vacuum, the residue taken up with a minimum of 2 *M* HNO_3, and the solution refrigerated. A dark green solid (*ca.* 2.3 g) was obtained which was filtered, washed with ethanol, and air-dried. Recrystallization was carried out by dissolving the solid in a minimum of 2 *M* HNO_3 at 35°, filtering, and refrigerating the filtrate overnight. The resulting green solid was filtered, washed with ethanol, and stored over $CaCl_2$ in the refrigerator (yield *ca.* 1.2 g). The solubility of the salt is *ca.* 1 g/ml in H_2O or dilute HNO_3, and it dissolves to give acidic solutions (pH ~2.2). Solutions are unstable at pH >5 at room temperature and under intense light. *Anal.* Calcd for $\{[Co(C_6H_9O_2N_3)(C_6H_8O_2N_3)]_2O_2\}(NO_3)_3 \cdot 2H_2O$ (990.56): Co, 11.89; C, 29.1; N, 21.15; H, 3.83; NO_3^-, 18.7; wt loss *in vacuo* (H_2O), 3.64. Found: Co, 11.52; C, 28.0; N, 20.92; H, 3.68; NO_3^-, 19.15; wt loss *in vacuo*, 3.61.

Preparation of μ-Superoxo-bis[bis(L-histidinato)cobalt(III)] Trichloride.—The preparation of the chloride salt was identical with that of the nitrate except that elution of the Dowex-50 column was carried out with various concentrations of HCl. The dark green band was removed with 6 *M* HCl, the eluent was evaporated, and the solid obtained was recrystallized from 1 *M* HCl at 35°. *Anal.* Calcd for $\{[Co(C_6H_9O_2N_3)(C_6H_8O_2N_3)]_2O_2\}Cl_3 \cdot 4H_2O$: Co, 12.45; C, 30.45; N, 17.75; H, 4.44; Cl, 11.25;

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

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[3] J. A. Weil and J. K. Kinnaird, *Inorg. Nucl. Chem. Lett.*, **5**, 251 (1969).

[4] Y. Sano and H. Tanabe, *J. Inorg. Nucl. Chem.*, **25**, 11 (1963).

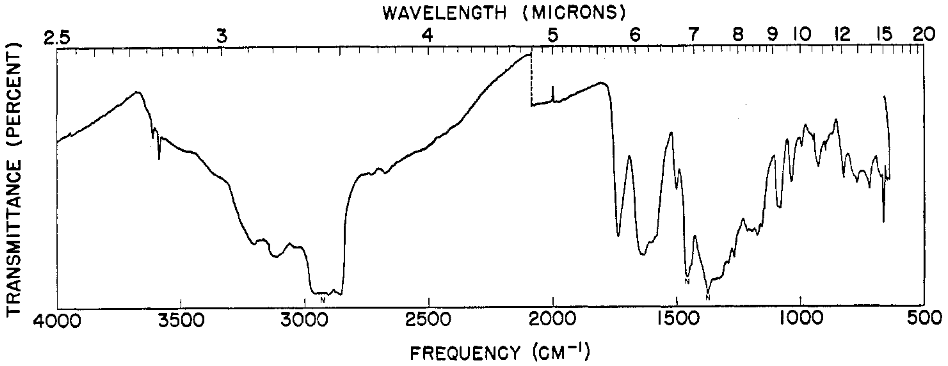

Figure 1.—The infrared spectrum of μ-superoxo-bis[bis(L-histidinato)cobalt(III)] trinitrate in a Nujol mull (Nujol peaks are marked N).

wt loss *in vacuo* (H_2O), 7.61. Found: Co, 11.92; C, 29.24; N, 17.45; H, 4.45; Cl, 11.25; wt loss *in vacuo*, 7.8.

Preparation of μ-Amido-μ-superoxo-bis[bis(ethylenediamine)-cobalt(III)] Tetranitrate Dihydrate.—The μ-amido-μ-superoxo-bis[bis(ethylenediamine)cobalt(III)] tetranitrate dihydrate used for comparison in the magnetic studies was specially prepared to prevent contamination with diamagnetic μ-amido-μ-nitrito complex.[5,6] The observed molar absorbance coefficients ϵ_{687} 486 and ϵ_{467} 527 agreed well with those reported by Stevenson and Sykes.[6]

Molecular Weight Determination. (1) **Redox Titration.**—Several attempts were made to determine the equivalent weight of the superoxo nitrate salt through redox reactions with various reducing agents, *i.e.*, I^-, Fe^{2+}, thiosalicylic acid, and hydroquinone. The last proved to be most useful, and, although potentiometric titrations of the superoxo complex directly with hydroquinone did not produce satisfactory end points, it was found that the complex could be reacted with a known volume of standard hydroquinone solution (~0.05 *N* in 0.1 *M* HNO_3) and the excess titrated potentiometrically with standard $K_2Cr_2O_7$ (~0.04 *N*).[7] An equivalent weight of 1030 ± 30 was obtained. If there is a one-electron change at the bridging group, $O_2^- + e^- \rightarrow O_2^{2-}$, the equivalent weight is equal to the molecular weight [calcd for $\{[Co(C_6H_9O_2N_3)(C_6H_8O_2N_3)]_2O_2\}(NO_3)_3\cdot 2H_2O$, 990 g/mol].

(2) **Oxygen Release.**—It was found that treatment of aqueous solutions of the μ-superoxo-bis(L-histidinato)cobalt(III) complex with hydroquinone in ethanol at room temperature resulted in a quantitative release of the bridging oxygen. The gas evolved was measured in a specially designed vacuum line equipped with an automatic Toepler pump. Three determinations gave a molecular weight of 985 ± 15 for the complex. Mass spectrometric analysis of the gas showed it to be oxygen, with no observable amounts of CO_2.

Charge Determination.—To determine the charge of the cation,[8] an aqueous solution of the nitrate salt of the complex was placed on an ion-exchange column containing Dowex-50-X-2 [200–400 mesh, previously treated with alkaline peroxide (30% H_2O_2 added to 3 *M* NaOH), water, then 3 *M* HCl] and washed well with water. The eluent was titrated with standard 0.01 *M* NaOH and an equivalent weight of 319 ± 4 was obtained from three titrations. (The titration curves also indicated the presence of small amounts of free histidine.) Assuming a molecular weight of 990, equivalent weights of 495 should be obtained for a 2+ ion, 330 for a 3+, and 248 for a 4+. Thus a charge of 3+ is indicated for the complex ion.

Unpaired Spin Determination. Nmr Susceptibility Shift.—The molecular weight can also be estimated by comparing the solvent proton nmr peak position of a solution of the cobalt complex with that of the pure solvent.[9] In our work, two coaxial tubes were used (with spinning) in a Varian 220-MHz spectrometer. The observed shift is given in a first approximation by

$$\frac{\Delta\nu}{\nu} = \frac{4\pi}{3}\Delta\chi = \frac{4\pi}{3}\chi$$

since the magnetic field is parallel to the sample tube. Here χ is the volume susceptibility of the complex.

The histidine complex as well as the similar known complex $[(en)_2Co\text{-}\mu\text{-}(O_2,NH_2)\text{-}Co(en)_2](NO_3)_4\cdot 2H_2O$ (mol wt 690.34) was examined in the inner tube in slightly acidified (HNO_3) water containing *ca.* 4% of *tert*-butyl alcohol. Typical results obtained are shown below.

Complex	Concn, g/ml	$\Delta\nu(H_2O)$, Hz	$\Delta\nu(CH_3)$, Hz
en	0.02197	38.2	39.2
His	0.02206	33.9	28.9

It is known that the en complex has one unpaired electron per molecule, with a Zeeman splitting constant $g = 2.0387$.[10] Use of the Curie law $\chi = n[g^2\beta^2S(S+1)/3kT]$, where n is the number of molecules per milliliter, leads to a predicted shift of $\Delta\nu = 38.4$ Hz at 298°K. The deviation from the observed value may arise from the effects of nonzero electron spin density on the solvent protons, from magnetic anisotropy effects, and from the neglected contributions to χ arising from diamagnetic plus second-order paramagnetic terms. The use of the *tert*-butyl peaks as shift indicators should minimize the first of these.

For our purposes, we shall take the shifts as proportional to the Curie expression and use the methyl shift ratio

$$\frac{\Delta\nu_{en}}{\Delta\nu_{His}} = \frac{C_{en}}{M_{en}}\frac{M_{His}}{C_{His}}\frac{g_{en}^2}{g_{His}^2}$$

to estimate the molecular weight of the histidine complex. The value of $g_{His} = 2.0265$ is available from solution electron paramagnetic resonance measurements previously reported.[3] We find $M_{His} = 930$. This is sufficiently close to the value obtained by the more accurate chemical methods to establish that the histidine complex contains one unpaired electron per molecule. The results of several runs indicated a mean deviation of *ca.* 10% in M_{His}.

Optical Spectra.—The infrared spectra in Nujol mulls of both His·HCl·H_2O and the superoxo complex (Figure 1) were recorded with a Perkin-Elmer spectrophotometer, Model 421. Excellent agreement with the literature was obtained for the spectra of the free base hydrochloride.[11]

Visible spectra of both the nitrate and chloride salts in water were recorded on a Cary Model 14 spectrophotometer. The two characteristic peaks gave excellent Beer's law curves, with molar absorbance coefficients given below.

	λ, nm	ε, l. mol^{-1} cm^{-1}	λ, nm	ε, l. mol^{-1} cm^{-1}
Nitrate salt, (0.3–2.5) × 10^{-3} *M*	478	462	678	693
Chloride salt, (0.4–2.3) × 10^{-3} *M*	478	461	680	676

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[5] R. Davies, M. Mori, A. G. Sykes, and J. A. Weil, *Inorg. Syn.*, **12**, 208 (1970).

[6] M. B. Stevenson and A. G. Sykes, *J. Chem. Soc. A*, 2293, 2979 (1969).

[7] I. M. Kolthoff, *Recl. Trav. Chim. Pay-Bas*, **45**, 745 (1926).

[8] For example, see H. H. Cady and R. E. Connick, *J. Amer. Chem. Soc.*, **80**, 2646 (1958).

[9] H. J. Friedrich, *Z. Naturforsch. B*, **19**, 663 (1964), and references therein.

[10] A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, **13**, 1 (1971).

[11] V. Balice and T. Theophanides, *J. Inorg. Nucl. Chem.*, **32**, 1237 (1970).

Discussion

The chemistry and structural data for oxygen-carrying (μ-peroxo) cobalt–histidine complexes and related substances have been previously summarized.[10] In the present work, we have characterized the first known μ-superoxo-dicobalt ion containing histidine as ligands. The presence of this bridge is clearly indicated by both the optical spectrum (678-nm peak) and the epr characteristics.[10]

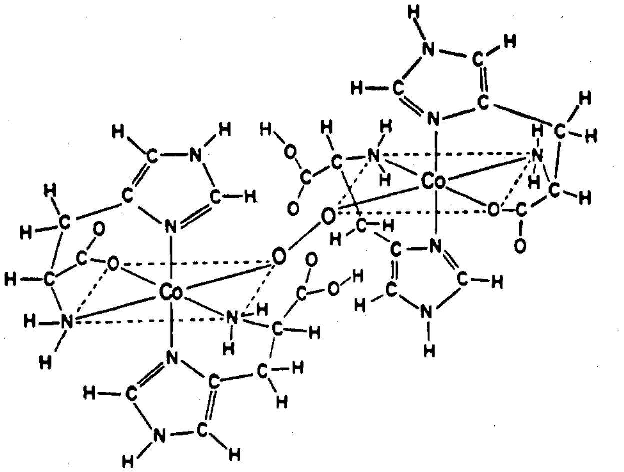

Figure 2.—The proposed structure of the μ-superoxo-bis[bis(L-histidinato)cobalt(III)](3+) ion.

The probable structure for the ion is shown in Figure 2, with the nitrogen atoms from the amine groups occurring cis to each other on each cobalt.[10,12]

Of particular interest in the infrared spectrum of the complex (Figure 1) is the strong band at 1740 cm^{-1} in the carbonyl region. This can be assigned to free carboxylic acid groups,[11] indicating that not all the histidine ligands are tridentate. The acidity of the complex dissolved in water also attests to the presence of such groups.

The reduction in acidic solution presumably goes *via* the one-electron step

$$[\mathrm{Co^{3+}O_2^{-}Co^{3+}}] + \mathrm{HQ} \longrightarrow [\mathrm{Co^{3+}O_2^{2-}Co^{3+}}] + \mathrm{HQ^{+}}$$

which is followed by internal charge transfer and oxygen release

$$[\mathrm{Co^{3+}O_2^{2-}Co^{3+}}] \longrightarrow 2\mathrm{Co^{2+}} + \mathrm{O_2}$$

The latter process is known to occur with the μ-peroxo-dicobalt–ammine complex.[10]

Qualitative experiments indicate that D-histidine, DL-histidine, and histamine can also form superoxo-bridged dicobalt complexes.

Acknowledgment.—We are very indebted to J. C. Sullivan for his excellent advice throughout this project and to S. S. Danyluk and N. Angerman for their patient help with the nmr measurements. Our gratitude also goes to the Argonne Analytic Staff (K. J. Jensen, I. M. Fox, A. Venters, A. M. Essling, and A. Engelkemeir) for their invaluable assistance.

(12) M. M. Harding and H. A. Long, *J. Chem. Soc. A*, 2554 (1968).

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Photoelectron Spectroscopy of Coordination Compounds. III. A Comparison of Platinum(II) and Platinum(IV) Compounds

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Received September 27, 1971

We have previously published two reports[1,2] that describe the use of photoelectron spectroscopy to investigate the π-acceptor character of ligands in coordination compounds.[3] In our first study[1] we found that the 2p binding energy of phosphorus in triphenylphosphine does not increase upon coordination of the triphenylphosphine to nickel, palladium, or cadmium. We ascribe this to the fact that a coordinated phosphorus atom not only donates an electron lone pair to a ligand–metal σ bond but also accepts a compensating amount of charge from the metal *via* π bonding. Similar neutralization of electron transfer between platinum and phosphorus of triphenylphosphine was inferred by Cook, *et al.*,[4] for $\mathrm{Pt[P(C_6H_5)_3]_4}$ in their comparison of Pt 4f binding energies for platinum coordinated to a number of π-bonding ligands. More recently we have presented more definitive arguments regarding the π-acceptor nature of ligands in a report on the inner-orbital shifts of both the metal and the ligand in a series of palladium complexes.[2] For those complexes containing only halide ligands, which are not π acceptors,[5] we observed that the palladium 3d binding energy is proportional to the palladium charge, estimated by means of electronegativity differences. For those complexes containing cyano ligands, which are known to be effective π-acceptor ligands,[6] the palladium 3d binding energy was found to be considerably larger than expected from simple charge calculations.

In the present paper we have examined some potassium salts of four- and six-coordinated platinum compounds in an effort to compare platinum chemical shifts with the shifts previously measured for the palladium compounds.[2] In addition, shifts were measured for the metal and the ligands in halo–cyano and halo–nitro complexes, in which the halides are σ donors and the cyano or nitro groups are π acceptors as well as σ donors. Data on such mixed-ligand compounds, when compared with data on complexes containing only one type of ligand, may provide a better understanding of ligand–metal bonding. The two series of compounds used for these mixed-ligand studies

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(1) J. R. Blackburn, R. Nordberg, F. Stevie, R. G. Albridge, and M. M. Jones, *Inorg. Chem.*, **9**, 2374 (1970).

(2) G. Kumar, J. R. Blackburn, R. G. Albridge, W. E. Moddeman, and M. M. Jones, *ibid.*, **11**, 296 (1972).

(3) L. D. Pettit, *Quart. Rev., Chem. Soc.*, **25**, 1 (1971).

(4) C. D. Cook, K. Y. Wan, U. Gelius, K. Hamrin, G. Johansson, E. Olsson, H. Siegbahn, C. Nordling, and K. Siegbahn, *J. Amer. Chem. Soc.*, **93**, 1904 (1971).

(5) The halide ligands do have available empty d orbitals for back-bonding; however, metal electron delocalization into these π-acceptor orbitals is small. For this reason the halides are considered to be only σ-donor ligands.

(6) L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963); **3**, 1581 (1964), and references therein.