With the assumption that the π-cyclopentadienyl ligand is regarded as formally tridentate by the occupation of three coordination sites, each cobalt atom may be regarded as possessing an octahedral-like coordination. The S–Co–S bond angles vary from 81 to 97° with an average value of 90°. All the Co–S distances in molecule I vary from only 2.18 to 2.25 Å with an average value of 2.21 Å. The average values for Co–$S^3$ (2.23 Å), Co–$S^2$ (2.21 Å), and Co–$S^1$ (2.19 Å) are not significantly different from one another. As expected, the observed Co–S–Co and Co–S–S bond angles in molecule I reflect considerable distortion of the tetrahedral-like (or pyramidal) character of each sulfur atom. The Co–S–Co bond angles vary in molecule I from 92 to 114° with an average value of 103°; the Co–S–S angular range is from 102 to 110° with an average value of 105°.

With no direct metal–metal interactions present in this complex, the molecular geometry is dictated primarily by the stereochemical requirements of the sulfur and disulfide ligands interconnecting the four [$Co_4$(π-$C_5H_5)_4(S_2)_x(S)_{4-x}$]. In view of the structure and stability of this complex, one is led to postulate the possible isolation of the other four related complexes [$(C_5H_5)_4$-$Co_4(S_2)_x(S)_{4-x}$] (where $x$ has the values 0, 1, 3, 4), each of which would also achieve a closed-shell electronic configuration for each metal atom without the need of cobalt–cobalt bonds. Nevertheless, the existence of such complexes must certainly depend upon the steric requirements of the resulting cobalt–sulfur fragment such that nonbonding repulsions, especially those between metal atoms, are minimized.

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# Organometallic Chalcogen Complexes. XVII. Preparation and Structural Characterization of a Metal–Oxygen Atom Cluster System, $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$[1]

**Vernon A. Uchtman[2] and Lawrence F. Dahl**

*Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.* *Received December 11, 1968*

**Abstract:** A new metal–oxygen cluster system, $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$, has been isolated in very low yield from prolonged ultraviolet irradiation of a $Co(\pi\text{-}C_5H_5)(CO)_2$ solution. The compound presumably arises by oxidative and/or photolytic decomposition of the King compound $Co_3(\pi\text{-}C_5H_5)_3(CO)_3$. The characterization of this complex was achieved from the X-ray structural determination. The molecular configuration of $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ consists of an equilateral triangle of cobalt atoms with triply bridging carbonyl and oxygen ligands symmetrically positioned above and below the tricobalt plane on the principal threefold molecular axis. The three cyclopentadienyl rings are perpendicularly disposed about the tricobalt plane such that with the assumption of cylindrical symmetry for each ring the molecule approximates $C_{3v}$-3m symmetry. A stereochemical consequence of the necessity of electron-pair cobalt–cobalt bonds in order for each cobalt atom to attain a closed-shell electronic configuration is a single-bond Co–Co distance of 2.365 ± 0.004 Å which is similar to the metal–metal bond length of 2.358 ± 0.002 Å in the electronically equivalent and structurally analogous complex $Ni_2Co(\pi\text{-}C_5H_5)_3(CO)_2$. The structural features of $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ are also compared with those of the geometrically related $Ni_3(\pi\text{-}C_5H_5)_3(CO)_2$ and $Ni_3(\pi\text{-}C_5H_5)_3S_2$ complexes. Despite complications caused by a twinning of the hexagonal crystals and by a horizontal mirror plane crystal disordering of the cyclopentadienyl, carbonyl, and oxygen ligands, the structure was successfully elucidated by application of the Wei technique and refined by least squares to a final $R_1(F^2)$ value of 6.4% and $R_2(F^2)$ value of 10.4% for the diffractometry-collected intensity data. The single-crystal component contains two formula species in a hexagonal unit cell of symmetry $P6_3/m$ and dimensions $a$ = 9.077 ± 0.006 Å and $c$ = 10.235 ± 0.006 Å; the calculated and observed densities are both 1.89 g $cm^{-3}$.

The pyrolysis or photolysis of mononuclear and dinuclear cyclopentadienylmetal carbonyl complexes has given rise to a number of unusual polynuclear cyclopentadienylmetal carbonyl complexes. The pyrolysis of $Fe_2(\pi\text{-}C_5H_5)_2(CO)_4$ yields the very stable tetranuclear iron derivative $[Fe(\pi\text{-}C_5H_5)CO]_4$,[3] while the pyrolysis of $Ni_2(\pi\text{-}C_5H_5)_2(CO)_2$ gives the stable paramagnetic trinuclear nickel complex $Ni_3(\pi\text{-}C_5H_5)_3$-$(CO)_2$.[4] Of considerable interest is the photolysis of $Rh(\pi\text{-}C_5H_5)(CO)_2$ which not only produces the dinuclear rhodium derivative $Rh_2(\pi\text{-}C_5H_5)_2(CO)_3$ but also on prolonged irradiation yields a mixture of two geo-

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[1] Previous paper in this series: V. A. Uchtman and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 3756 (1969).

[2] This manuscript is based in part on a dissertation submitted by V. A. Uchtman to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, July 1968.

[3] R. B. King, *Inorg. Chem.*, **5**, 2227 (1966).

[4] E. O. Fischer and C. Palm, *Chem. Ber.*, 91, 1725 (1958).

metrical isomers of the trinuclear rhodium complex $Rh_3(\pi\text{-}C_5H_5)_3(CO)_3$.[5] X-Ray diffraction studies[6,7] showed that both isomers contain a triangular array of bonding rhodium atoms; one of the isomers[6] of $C_{3v}$ symmetry possesses three doubly bridging carbonyls with each bridging a different pair of rhodium atoms, while the other isomer[7] has a terminal carbonyl coordinated to one rhodium atom and two doubly bridging carbonyls connecting the other two rhodium atoms. From the photolysis of $Co(\pi\text{-}C_5H_5)(CO)_2$, King[3] successfully prepared the cobalt analog $Co_3(\pi\text{-}C_5H_5)_3(CO)_3$ and found from an infrared study that it seems to exist in two isomeric configurations. However, this infrared analysis indicated that triply bridging carbonyl groups are present in at least one of the cobalt isomers. This structural difference is not surprising especially in light of the molecular structures of $[Fe(\pi\text{-}C_5H_5)CO]_4$[8] and $Ni_3(\pi\text{-}C_5H_5)_3(CO)_2$,[9] both of which were found to possess triply bridging carbonyl groups.

In an effort to obtain crystals of $Co_3(\pi\text{-}C_5H_5)_3(CO)_3$ suitable for X-ray diffraction analysis, a new black trinuclear cobalt complex was obtained. The complete crystal structure analysis along with additional chemical and physical evidence has established the identity of this complex as $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$. This compound presumably is identical with the uncharacterized black compound obtained in low yield by King[3] upon the heating of a sample of $Co_3(\pi\text{-}C_5H_5)_3(CO)_3$ in a boiling toluene–methylcyclohexane solution.

## Experimental Procedure

**Preparation of $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$.** In an attempt to prepare a sample of $Co_3(\pi\text{-}C_5H_5)_3(CO)_3$, the procedure originally reported by King[3] was repeated with some modifications. Two grams of $Co(\pi\text{-}C_5H_5)(CO)_2$ in 50 ml of hexane was placed under nitrogen in a quartz tube. The stirred reaction mixture was irradiated for 6 days with a Nester–Faust low-pressure ultraviolet light source operated with an aluminum foil reflector at 35 W and placed at a distance of 30 cm from the quartz vessel. The solution was filtered, and the black residue washed with 25 ml of hexane and dried under vacuum. The resulting black powder was then dissolved in a 10% excess of dichloromethane; a quantity of hexane equal to one-fourth the total solution volume was added, and the solution was evaporated very slowly over $P_2O_5$ in an evacuated desiccator. After 2 days the solvent had completely dried leaving about 10 mg of well-formed rod-shaped crystals of hexagonal cross section; these crystals were hand-picked from the surrounding decomposition product. An infrared spectrum of this compound ($CH_2Cl_2$ solution) exhibited a single carbonyl stretching frequency at 1720 $cm^{-1}$. The extremely low yield and small amount of compound available prevented magnetic susceptibility or proton nmr measurements. The formulation of this compound as $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ was mainly accomplished by the crystal structure determination and substantiated by the following elemental analysis. *Anal.* Calcd for $Co_3C_{16}H_{15}O_2$: C, 46.2; H, 3.9. Found: C, 46.0; H, 3.6.

All reactions and recrystallizations were carried out in an atmosphere of dry, prepurified nitrogen. $Co(\pi\text{-}C_5H_5)(CO)_2$ was used as obtained from the supplier (Alfa Inorganics, Inc.). All solvents were of reagent grade and were dried by standard procedures before use. Infrared spectra were recorded on a Beckman IR-8 spectrometer. Analyses were performed by Alfred Bernhardt, Max Planck Institut, Mülheim (Ruhr), West Germany.

**X-Ray Data Collection.** A single crystal of $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ suitable for X-ray analysis was obtained by the procedure described above. A regular crystal of hexagonal cross section (maximum cross-sectional diameter 0.25 mm) and of length 0.15 mm was mounted with epoxy cement on a thin glass fiber such that the crystallographic *c* (unique) axis was the axis of rotation. Preliminary X-ray oscillation and Weissenberg photographs indicated that the crystal belonged to the hexagonal system, Laue symmetry $D_{6h}$-6/m 2/m 2/m. After optical alignment of the crystal on a General Electric four-circle automated diffractometer, 36 reflections were carefully centered;[10] the angle settings obtained for these reflections were used to calculate lattice constants and angle settings for all other reflection data. The collection and treatment of intensity data followed closely the procedures described previously[1] except that 20-sec background counts were used. Intensity data ($hkl$, $\bar{h}kl$) corresponding to six equivalent forms of hexagonal $D_{6h}$ data were collected out to a $2\theta$ value of 45°, beyond which there were only a few reflections with intensities above background. Ten low-angle reflections had intensities which exceeded the linear limits of the pulse height analyzer. The measurement of these intensities was repeated with Zr-foil attenuators placed between the crystal and the counter. The proper scale factor necessary to merge these intensities with the other data was obtained by the measurement with and without attenuation of the intensities of several sets of standard reflections. A total of 855 observed and 189 unobserved (*i.e.*, $I < 2\sigma(I)$) reflections were obtained. The intensity variation in equivalent reflections was generally no greater than 5%, and therefore all equivalent forms of data were averaged to give 192 independent observed intensity maxima. No extinction, dispersion, or absorption corrections were made. The real and imaginary anomalous dispersion corrections for Mo K$\alpha$ radiation are sufficiently small (*i.e.*, $\Delta f' = -0.4$, $\Delta f'' = 1.1$ for Co)[11] that any effect on the molecular parameters should be negligible. The variation of absorption correction factors with $\theta$ is negligible for the measured $\mu R$ value ($\mu R_{max} \leq 0.45$).[12]

**Unit Cell and Space Group.** The measured constants (25°) for the hexagonal unit cell of $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ are $a = 9.077 \pm 0.006$ Å, $c = 10.235 \pm 0.006$ Å; the volume of the unit cell equals 730.3 Å$^3$. The experimental density of 1.89 g $cm^{-3}$ (determined by flotation in a series of 1,2-dibromopropane–2-iodopropane solutions) agrees with that of 1.89 g $cm^{-3}$ calculated on the basis of two formula species per unit cell. The linear absorption coefficient for Mo K$\alpha$ radiation ($\lambda$ 0.7107 Å) is 34.9 $cm^{-1}$. The total number of electrons, $F(000)$, is 208.

The systematic absences of $l$ odd for $\{000l\}$, indicative of a $6_3$ axis in the *c* direction, uniquely define the apparent space group as $P6_322$-($D_{6h}^6$).[13] A trial model which conformed to the observed $D_{6h}$ Laue symmetry and Patterson vector requirements (described in the next section) was based on an incoherent twinning mechanism involving a hexagonal single crystal of symmetry $P6_3/m$-($C_{6h}^2$),[14] which itself results from a crystal disordering of the carbon and oxygen atoms (*vide infra*). Consistent with the requirements of the space group $P6_3/m$, the six cobalt atoms in the unit cell occupy one set of the following sixfold special positions (6h): $\pm(x, y, {}^1/_4; -y, x - y, {}^1/_4; y - x, -x, {}^1/_4)$; the four carbonyl oxygen half-atoms, the four carbonyl carbon half-atoms, and the four oxo oxygen half-atoms occupy three sets of the fourfold special positions (4f): $\pm({}^1/_3, {}^2/_3, z; {}^2/_3, {}^1/_3, {}^1/_2 + z)$; while the 60 carbon half-atoms of the six disordered cyclopentadienyl groups occupy five sets of the following general 12-fold positions (12i): $\pm(x, y, z; -y, x - y, z; y - x, -x, z; x, y, {}' - z; -y, x - y, {}^1/_2 - z; y - x, -x, {}^1/_2 - z)$. Thus, the solution of the structure required the location of one cobalt atom, one half-weighted carbonyl group, one half-weighted oxygen atom, and one half-weighted cyclopentadienyl group.

**Determination of the Structure.** On the basis of the observed $D_{6h}$ symmetry for the reciprocal lattice, a three-dimensional Patterson synthesis which utilized the observed structure factor ampli-

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(5) E. O. Fischer and H. Schuster-Woldan, cited in ref 6.

(6) O. S. Mills and E. F. Paulus, *J. Organometal. Chem.*, 10, 331 (1967).

(7) E. F. Paulus, E. O. Fischer, H. P. Fritz, and H. Schuster-Woldan, *ibid.*, 10, P3, (1967).

(8) M. Neuman, R. B. King, and L. F. Dahl, submitted for publication.

(9) A. A. Hock and O. S. Mills, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Proceedings of the 6th International Conference on Coordination Chemistry, Detroit, Mich., 1961, p 640.

(10) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(11) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215.

(12) "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, p 295.

(13) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 289.

(14) See ref 13, p 283.

tudes was calculated. All significant interatomic vector peaks due to the heavy atoms were found to lie on the Harker sections $P(u, v, 0)$ and $P(u, v, {}^1/_2)$. The $P(u, v, 0)$ Harker section was consistent with the six cobalt atoms being arranged in two symmetry-related equilateral triangles of approximate Co–Co lengths 2.4 Å. However, the cobalt–cobalt vectors found in the Harker section $P(u, v, {}^1/_2)$ were not consistent with any of the special sixfold sets of positions (necessary for two triangular $Co_3$ clusters per unit cell) contained in the apparent space group $P6_322$. Instead, the cobalt-cobalt vectors of the Patterson map could be explained on the basis of the space group $P6_3/m$. In order to do this, the observed Patterson map of $D_{6h}$ symmetry must be assumed to be the superposition of two other Patterson maps, each of $C_{6h}$ symmetry. One of these maps consists of the interatomic vectors from a set of six cobalt atoms which are located in the following sixfold set of special positions of space group $P6_3/m$: $\pm(x, y, {}^1/_4;\ -y, x - y, {}^1/_4;\ y - x, -x, {}^1/_4)$. The other Patterson map is made up of vectors from six cobalt atoms which are in positions exactly related to the above sixfold set of special positions by a symmetry operation such as a ⟨100⟩ mirror plane or ⟨100⟩ twofold rotation axis. This set of positions [*i.e.*, $\pm(y, x, {}^1/_4);\ -x, y - x, {}^1/_4;\ x - y, -y, {}^1/_4)$] can be generated from the first set by an exchange of $x$ and $y$. It has previously been demonstrated[15,16] that a crystal which is in fact a twinned composite will give rise to a Patterson map which is a superposition of interatomic vector maps from the individual single crystal components. For the hexagonal crystal in question a twinning operation such as a ⟨100⟩ mirror plane or ⟨100⟩ twofold rotation axis operating on the reciprocal lattice of a single crystal of $C_{6h}$ symmetry would generate a twinned composite with the same hexagonal unit cell but of the observed $D_{6h}$ symmetry; such a twinned composite would also produce the observed $D_{6h}$ Patterson interatomic vector map. That an incoherent twinning mechanism is operative rather than a coherent disorder phenomenon is made apparent by the absence of any peaks on this Patterson map attributable to interatomic vectors between alternate positions of metal atoms disordered in the unit cell. Such peaks have previously been observed on Patterson maps computed during the course of structural analyses on the disordered crystals of $Fe_3(CO)_{12}$[17,18] and $Co_4(CO)_{12}$[17] but have not been present on the Patterson maps of $Rh_4(CO)_{12}$[15,16] whose crystals were found to exhibit incoherent twinning.

The determination of the carbon and oxygen positions in this incoherently twinned crystal was accomplished by the Wei procedure,[15,16] which permitted a breakdown of the observed $|F(hkl)|^2$ data for the twinned composite into the $|F(hkl)'|$ and $|F(khl)'|$ coefficients of the single-crystal component (of assumed $P6_3/m$ symmetry), a procedure necessary for the calculation of the Fourier syntheses. For any of the possible twinning operations mentioned above, the two hexagonal reciprocal lattices of $C_{6h}$-6/m point group symmetry superimpose such that the observed and calculated intensities for the twinned hexagonal reciprocal lattice of $D_{6h}$-6/m2/m2/m point group symmetry are related to the corresponding quantities of the untwinned $C_{6h}$ reciprocal lattices by the relationships

$$|F(hkl)_o|^2 = m|F(hkl)_o'|^2 + (1 - m)|F(khl)_o'|^2 \quad (1)$$

$$|F(hkl)_c|^2 = m|F(hkl)_c'|^2 + (1 - m)|F(khl)_c'|^2 \quad (2)$$

where $m$ represents the fraction of one $C_{6h}$ component lattice; for the observed symmetry to be $D_{6h}$ $m$ must be equal to 0.5. In order to estimate the magnitudes of the structure factors $F(hkl)_o'$ and $F(khl)_o'$ for the untwinned $P6_3/m$ space group, the observed values $|F(hkl)_o|^2$ were apportioned according to the Wei procedure[15,16] as follows

$$|F(hkl)_o'| = \left[|F(hkl)_o|^2\frac{|F(hkl)_c'|^2}{|F(hkl)_c|^2}\right]^{1/2} \quad (3)$$

$$|F(khl)_o'| = \left[|F(hkl)_o|^2\frac{|F(khl)_c'|^2}{F(hkl)_c|^2}\right]^{1/2} \quad (4)$$

where the $F_c$ values were obtained from the estimated positions of the cobalt atoms determined from the Patterson map. A difference Fourier synthesis, computed with coefficients calculated in this manner, revealed the approximate positions of cyclopentadienyl carbon atoms; the only other chemically significant peaks were four very broad peaks which were located on the two threefold axes of space group $P6_3/m$. These four peaks were disposed such that one was directly above and one was directly below the centroid of each of the two cobalt triangles; for any one triangle the peak-center to cobalt distance (for all three cobalt atoms) was about 2 Å. Only one of these peaks was crystallographically independent, the other three being generated by the symmetry elements of the space group. This peak and its symmetry-related one on the opposite side of each $Co_3$ triangle were originally interpreted as being due to the electron density of two triply bridging carbonyl groups. Least-squares refinement of this presumed model of molecular composition $Co_3(\pi\text{-}C_5H_5)_3(CO)_2$ led to convergence; nevertheless, the isotropic thermal parameter of the crystallographically independent carbonyl oxygen atom remained at an unusually high value relative to those of the other atoms (*i.e.*, the least-squares determined isotropic $B$ value for the carbonyl oxygen atom was 10.8 Å$^2$ compared to 2.3 Å$^2$ for the carbonyl carbon atom); the refined carbon–oxygen distance of 0.90 Å was also completely unrealistic. Therefore, the difference Fourier map was carefully reexamined, and the intensity of the one independent broad peak along the threefold axis was plotted as a function of the $z$ coordinate. This plot (Figure 1) revealed that the asymmetric peak shape (indicative of two partially resolved peaks) could best be explained as being due to the superposition of one triply bridging carbonyl group bonded to one side of the $Co_3$ fragment and another triply bridging nonhydrogen atom (possibly with hydrogen atoms bonded to it) located on the opposite side of the $Co_3$ unit at a bonding distance approximately equal to that of the carbonyl carbon atom. After a thorough consideration of possible modes of formation of the complex *via* initial photolysis of $Co(\pi\text{-}C_5H_5)(CO)_2$ together with the compound's carbon–hydrogen analysis and infrared spectrum (see Discussion), this additional atom was determined to be a triply bridging oxygen atom. Thus, the two partially resolved peaks on the difference Fourier synthesis were explained as follows. The peak of highest intensity, located approximately 1.9 Å from the cobalt atoms, is attributed to the superposition of electron density of the carbonyl carbon half-atom and the oxygen half-atom, while the weaker peak (which appears as a shoulder with about one-half the intensity of

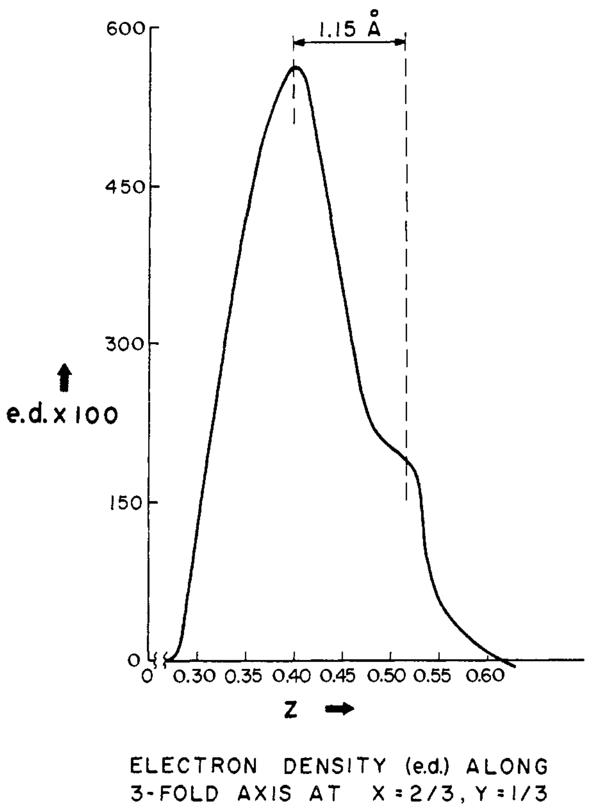

Figure 1. Electron density along the threefold axis at $x = {}^2/_3$, $y = {}^1/_3$ of the hexagonal unit cell of $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$.

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[15] C. H. Wei, Abstracts of Papers, National Meeting of the American Crystallographic Association, University of Minnesota, Minneapolis, Minn., Aug 20–25, 1967, p 83.

[16] *Cf.* C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 4792 (1967).

[17] C. H. Wei and L. F. Dahl, *ibid.*, **88**, 1821 (1966).

[18] C. H. Wei and L. F. Dahl, *ibid.*, **91**, 1351 (1969).

the larger one and about 1.2 Å from it) is due to the electron density of the carbonyl oxygen half-atom.

The superposition of the carbonyl group and the oxygen atom, as well as an observed twofold disorder of the cyclopentadienyl carbon atoms, is expected due to the centrosymmetric nature of the difference Fourier map which had been calculated from a model of $C_{6h}$ symmetry. Attempts to refine the structure on the basis of the implied noncentrosymmetric space group $P6_3$ (necessary for an ordered arrangement of cyclopentadienyl, carbonyl, and oxo ligands) were unsuccessful. Instead, refinement was achieved in the centrosymmetric space group $P6_3/m$, which crystallographically demands not only a half-atom crystal disordering of the carbonyl groups and the oxo atoms but also a crystal disordering of the cyclopentadienyl groups.

The twinning-disorder model and nature of the structure was verified by full-matrix least-squares refinement. The function minimized was $\Sigma w[|F(hkl)_o|^2 - s^2|F(hkl)_c|^2]^2$ where $s$ is the single adjusted scale factor; the $|F(hkl)_c|^2$ values were obtained from eq 2, and weights were based on $w_i = 1/\sigma_i^2(F_o^2)$ where $\sigma_i(F_o^2) = 2F_o\sigma(F_o)$. In accord with the symmetry requirements imposed by the $P6_3/m$ space group on the disordered model, all carbon and oxygen atoms were given half their normal electron scattering weight. In this refinement (with space group symmetry $P6_3/m$) the independent cyclopentadienyl group was treated as a rigid half-weighted $C_5H_5$ ring (hydrogen atoms were included), while anisotropic thermal parameters were utilized for the cobalt atom only. (Table I gives a brief description of the rigid-body system[19] used.) During the course of the refinement the carbonyl carbon–oxygen distance was fixed at a value of 1.185 Å. That this value is reasonable can be seen by comparison with the structures[20] of $Ni_2Co(\pi\text{-}C_5H_5)_3(CO)_2$ and $Ni_3(\pi\text{-}C_5H_5)_3(CO)_2$ which both have C–O lengths of 1.183 Å and infrared carbonyl stretching frequencies of 1723 and 1729 cm$^{-1}$, respectively, compared to that of 1720 cm$^{-1}$ for $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$. Final discrepancy values based on this full-matrix rigid-body isotropic–anisotropic least-squares refinement are $R_1(F^2) = 6.4\%$ and $R_2(F^2) = 10.4\%$

$$R_1(F^2) = \frac{\Sigma||F(hkl)_o|^2 - s^2|F(hkl)_c|^2|}{\Sigma|F(hkl)_o|^2} \times 100 \qquad (5)$$

$$R_2(F^2) = \frac{\Sigma w||F(hkl)_o|^2 - s^2|F(hkl)_c|^2|}{\Sigma w|F(hkl)_o|^2} \times 100 \qquad (6)$$

where $|F(hkl)_c|^2$ was obtained from eq 2.

A final difference Fourier map with coefficients calculated from the final positional parameters (but with isotropic thermal parameters for all atoms) revealed no residual peaks greater than 1.6 e/Å$^3$ except in the region of the metal atoms; these more intense residual peaks were attributed to anisotropic thermal motion which was taken into account in the anisotropic–isotropic least-squares refinement.

The final atomic parameters from the output of the last least-squares cycle are given in Table I.[21] Interatomic distances and angles and their individual estimated standard deviations are given in Table II. The Blount program[22] was used to calculate all Patterson and Fourier functions. A local modification of the Busing-Martin-Levy ORFLS program[23] was used for all least-squares refinements. The atomic scattering factors used for all atoms were those compiled by Hanson, *et al.*[24]

**Table I.** Final Atomic Parameters with Their Standard Deviations from Rigid-Body Least-Squares Refinement for $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$

| | $x$ ($10^4\sigma_x$) | $y$ ($10^4\sigma_y$) | $z$ ($10^4\sigma_z$) | $B$ ($10\sigma_B$) |
|---|---|---|---|---|
| Co | 0.5123 (2) | 0.3251 (2) | $^1/_4$ | $a$ |
| C(1)$^b$ | $^2/_3$ | $^1/_3$ | 0.1381 | 3.6 (4) |
| O(1)$^b$ | $^2/_3$ | $^1/_3$ | 0.0223 | 4.9 (3) |
| O(2) | $^2/_3$ | $^1/_3$ | 0.3930 (19) | 3.5 (4) |
| C(2)$^c$ | 0.3219 | 0.3105 | 0.3667 | 5.2 (3) |
| C(3)$^c$ | 0.3835 | 0.4545 | 0.2859 | 3.4 (2) |
| C(4)$^c$ | 0.3554 | 0.3989 | 0.1554 | 4.4 (3) |
| C(5)$^c$ | 0.2764 | 0.2205 | 0.1556 | 4.4 (3) |
| C(6)$^c$ | 0.2557 | 0.1658 | 0.2862 | 4.3 (3) |
| H(C-2)$^e$ | 0.3249 | 0.3108 | 0.4732 | 8.0$^d$ |
| H(C-3)$^e$ | 0.4427 | 0.5862 | 0.3184 | 8.0$^d$ |
| H(C-4)$^e$ | 0.3889 | 0.4799 | 0.0692 | 8.0$^d$ |
| H(C-5)$^e$ | 0.2379 | 0.1388 | 0.0695 | 8.0$^d$ |
| H(C-6)$^e$ | 0.1983 | 0.0343 | 0.3189 | 8.0$^d$ |

[a] Anisotropic temperature factors of form $\exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}$ were used for the cobalt atom. The resulting thermal coefficients (with standard deviations of the last significant figure given in parentheses) are as follows: $B_{11}$, 0.0076 (3); $B_{22}$, 0.0087 (3); $B_{33}$, 0.0216 (3); $B_{12}$, 0.0039 (2); $B_{13} = B_{23} = 0$. [b] The carbonyl group (*i.e.*, atoms C(1) and O(1)) was defined as a rigid group with C(1)–O(1) = 1.185 Å. [c] The rigid group atomic positions for the cyclopentadienyl carbon atoms, C(2) through C(6), are defined relative to an orthonormal coordinate system $x'$, $y'$, $z'$ as follows. The origin of the coordinate system lies on the centroid of the ring, $+x'$ passes through one atom of the ring, and all atoms lie in the $x'y'$ plane. The rigid group angles $\phi$, $\theta$, and $\rho$ (given below with standard deviations of the last significant figure given in parentheses) define the orientation of the rigid group coordinate system with respect to the crystallographic axis system. The hydrogen atoms of the cyclopentadienyl ring lie along vectors extended from the ring centroid through the carbon atoms such that the ring conforms to $D_{5h}$ symmetry with C–C = 1.405 Å and C–H = 1.08 Å. The rigid group angles (deg) are: $\phi$, 183.7 (2); $\theta$, 180.1 (2); $\rho$, −88.62 (3). [d] The thermal parameters of the hydrogen atoms were not varied during the refinement. [e] This notation signifies the carbon atom to which the hydrogen atom is coordinated.

**Table II.** Intramolecular Distances (Å) and Angles (Deg) for $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$[a]

| | |
|---|---|
| Co–Co | 2.365 (4) |
| Co–C(carbonyl) | 1.78 (2) |
| Co–O(bridging) | 2.00 (1.5) |
| C(carbonyl)–O(carbonyl) | 1.18$^b$ |
| Co–C(cyclopentadienyl) | 2.07 (av) |
| Co–C(cyclopentadienyl centroid) | 1.69 |
| C(carbonyl)···O(bridging) | 2.61 (3.5) |
| Co···O(carbonyl) | 2.70 (2) |
| Co–Co–Co | 60.0 |
| Co–C(carbonyl)–O(carbonyl) | 130.0 (5) |
| Co–C(carbonyl)–Co | 83.1 (8) |
| Co–O(bridging)–Co | 72.4 (6) |
| O(bridging)–Co–C(carbonyl) | 87.0 (10) |
| C(carbonyl)–Co–Co | 48.4 (3) |
| O(bridging)–Co–Co | 53.8 (3) |

[a] Individual estimated standard deviations of the last significant figures are given in parentheses. [b] In the least-squares refinement the C–O bond was treated as a rigid group of length 1.185 Å.

## Discussion

The molecular configuration of $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ shown in Figure 2 consists of an equilateral triangle of bonding cobalt atoms with a cobalt–cobalt distance of 2.365 Å (indiv esd, 0.004 Å); to each cobalt atom there is attached a $\pi$-bonded cyclopentadienyl ring. A triply bridging carbonyl group and a triply bridging oxygen atom are symmetrically coordinated to opposite sides of the $Co_3$ fragment. The molecular geometry

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(19) *Cf.*, S. F. Watkins, Ph.D. Thesis (Appendix), University of Wisconsin, 1967, and references cited therein.

(20) V. A. Uchtman and L. F. Dahl, submitted for publication.

(21) A Table containing observed and calculated structure factors for $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ has been deposited as Document No. NAPS-00333 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by a citing of the document number and by the remitting of $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

(22) J. F. Blount, Ph.D. Thesis (Appendix), University of Wisconsin, 1965.

(23) W. R. Busing, K. O. Martin, and H. A. Levy, "OR FLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1962.

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approximates $C_{3v}$-3m symmetry. From a valence-bond viewpoint each of the three zerovalent cobalt atoms formally achieves a closed-shell electronic configuration by a contribution of five electrons from each cyclopentadienyl radical, $^2/_3$ electron from the carbonyl group, $^4/_3$ electrons from the oxo ligand (which thereby has its one remaining unshared electron pair located on the molecular threefold axis), and one electron from each of the other two cobalt atoms.

This compound represents one of the few known examples of an organometallic complex which contains a single oxygen atom triply bridging three transition metal atoms. Since it was found during the prolonged photolysis of a $Co(\pi\text{-}C_5H_5)(CO)_2$ solution, its formation presumably results from the photochemical or thermal decomposition of $Co_3(\pi\text{-}C_5H_5)_3(CO)_3$ which King[3] has shown to be the initial product of the photolysis of $Co(\pi\text{-}C_5H_5)(CO)_2$, in the presence of $O_2$. (The possibility of the oxygen atom originating from a carbonyl group cannot be excluded.) Although measures were taken to exclude atmospheric oxygen from the reaction vessel, trace amounts of $O_2$ could possibly have entered during the long reaction time. Fischer, *et al.*,[25] have shown that $O_2$ reacts quite easily with $Cr(\pi\text{-}C_5H_5)_2$ to produce $Cr_4(\pi\text{-}C_5H_5)_4(O)_4$.

Detailed chemical and physical characterization of $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ was hindered by the extremely low yield of the complex. Nevertheless, the infrared spectrum and the carbon–hydrogen analysis provide convincing evidence in support of the formulation of the compound's stoichiometry from the X-ray structural determination. As expected for a symmetrical triply bridging carbonyl group, the infrared spectrum exhibits only a single absorption band in the carbonyl stretching region at 1720 $cm^{-1}$ which is very close to the triply bridging frequencies of 1723 and 1729 $cm^{-1}$ observed for the complexes $Ni_2Co(\pi\text{-}C_5H_5)_3(CO)_2$ and $Ni_3(\pi\text{-}C_5H_5)_3(CO)_2$, respectively.[20] The carbon–hydrogen analysis eliminates all other possible formulas $Co_3(\pi\text{-}C_5H_5)_3(CO)(L)$ where L is CO, C, CH, or $CH_2$. Recently, Otsuka, Nakamura, and Yoshida[26] briefly reported the isolation of the complex $Co_3(\pi\text{-}C_5H_5)_3(CO)(S)$ which presumably differs from $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ only by the exchange of a congener sulfur atom for an oxygen atom. Other examples of two presumably isosteric complexes also differing only by the exchange of sulfur and oxygen are the corresponding molybdenum(V) complexes $[Mo(\pi\text{-}C_5H_5)(O)]_2S_2$[27,28] and $[Mo(\pi\text{-}C_5H_5)(O)]_2O_2$[29] which contain doubly bridging chalcogen atoms, and the cyclopentadienylchromium complexes $Cr_4(\pi\text{-}C_5H_5)_4(S)_4$[30] and $Cr_4(\pi\text{-}C_5H_5)_4(O)_4$.[25] The molecular geometry of these latter two electronically equivalent analogs has been proposed to consist of a tetrahedron of chromium atoms with oxygen (or sulfur) atoms triply bridging each triangular face of three single-bonded chromium atoms.[31]

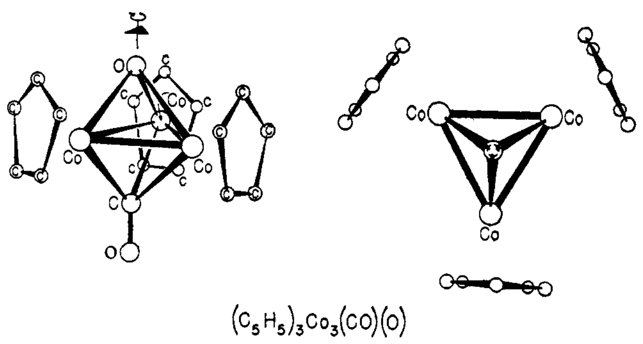

Figure 2. Molecular configuration of $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$.

The solution of the crystal structure was complicated by a half-atom disorder of the carbonyl and oxo groups together with a half-atom disorder of the cyclopentadienyl groups such that the molecular symmetry indicated by the X-ray diffraction data was $D_{3h}$-$\bar{6}$2m. Similar half-atom crystal disorders of carbonyl and nitrosyl groups as well as single atoms are not uncommon and have been observed in a number of compounds, for example, in the crystal structures of $[FeNOBr(das)_2]ClO_4$[32] ("das" denotes *o*-phenylenebis(dimethylarsine)), where the bromine atom and nitrosyl group are disordered by a crystallographic center of symmetry, and $[(C_6H_5)_3P]_2Rh(CO)Cl$,[33] where the CO and Cl are disordered by a crystallographic center of symmetry. Corresponding half-atom disorders of cyclopentadienyl rings have also been previously found in $Ni_3(\pi\text{-}C_5H_5)_3(CO)_2$[9,20] and $Ni_2Co(\pi\text{-}C_5H_5)_3(CO)_2$[20] (where the disorder of the cyclopentadienyl rings is also not imposed by any crystallographic symmetry elements) and $Ni_3(\pi\text{-}C_5H_5)_3S_2$[34] (where the cyclopentadienyl rings are located in positions exactly analogous to those in $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$). This crystalline disorder has necessarily decreased the accuracy of the determination of the positions of these atoms, and therefore the errors involved in the interatomic distances and angles involving these atoms are greater than one would like. An additional complexity was imposed by a presumed twinning of the hexagonal unit cell such as to increase the observed Laue symmetry from $C_{6h}$-6/m to $D_{6h}$-6/m2/m2/m. This same twinning phenomenon was later observed in the crystal structure of the closely related complex $Ni_3(\pi\text{-}C_5H_5)_3S_2$;[34] a crystallographic treatment nearly identical with that applied here successfully elucidated its molecular structure.

The packing of the two $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ molecules in the hexagonal unit cell of $P6_3/m$ symmetry is illustrated in Figure 3. With the assumption of cylindrical symmetry for each cyclopentadienyl ring, the crystal data for $Ni_3(\pi\text{-}C_5H_5)_3(CO)_2$, $Ni_2Co(\pi\text{-}C_5H_5)_3(CO)_2$, $Ni_3(\pi\text{-}C_5H_5)_3S_2$, and $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ are all very similar. The hexagonal space group symmetry in each case is $P6_3/m$ and the hexagonal lattice constants are found in the following ranges: *a*, 9.08–9.59 Å; *c*, 9.92–10.74 Å. The orientations of the $M_3$ triangles in the hexagonal unit cell (illustrated for $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ in Figure 3) are all nearly identical. For all four of these complexes it is difficult to assess the in-

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[26] S. Otsuka, A. Nakamura, and T. Yoshida, *Inorg. Chem.*, 7, 261 (1968).

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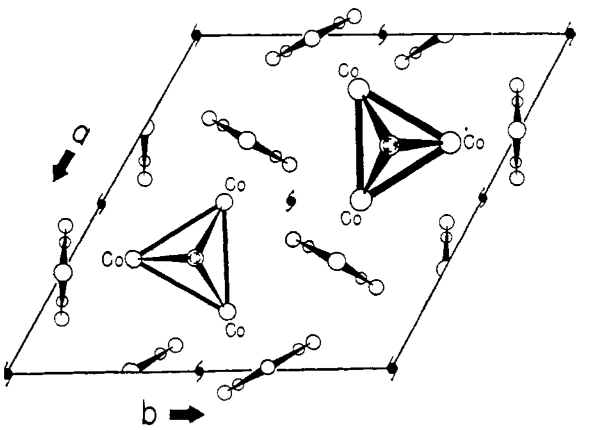

Figure 3. [001] projection of the untwinned hexagonal unit cell of $P6_3/m$ symmetry containing two $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ molecules each located on a threefold axis. The three cyclopentadienyl rings, the carbonyl group, and oxygen atom per molecule are randomly disordered in one of two orientations which are related by a crystallographic mirror plane.

fluence of the disordered cyclopentadienyl rings on the molecular packing. However, calculations based on ordered models show that in all cases the shortest H···H separations of range 2.4–2.5 Å compare favorably with the sum of van der Waals radii (2.4 Å).[35] These H···H contacts undoubtedly have a major effect on the molecular packing in that all other intermolecular interatomic lengths are greater than normal van der Waals contact distances.

The geometrical configuration of $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ is also very similar to that of $Ni_3(\pi\text{-}C_5H_5)_3(CO)_2$, $Ni_2Co(\pi\text{-}C_5H_5)_3(CO)_2$, and $Ni_3(\pi\text{-}C_5H_5)_3S_2$, all of which have the triply bridging ligands disposed on a threefold axis which passes through the center of the metal triangle. The Co–C–O angle of 130° in $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ resembles the analogous angles of 135° in $Ni_3(\pi\text{-}C_5H_5)_3(CO)_2$ and 134° in $Ni_2Co(\pi\text{-}C_5H_5)_3(CO)_2$. The Co–C(carbonyl)–Co angle of 83° in $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ compares with the corresponding angles of 75 and 76° in the latter two complexes, respectively, while the Co–O–Co angle of 72° parallels the corresponding Ni–S–Ni angle of 80° in $Ni_3(\pi\text{-}C_5H_5)_3S_2$. These acute angles subtended at the apical chalcogen atoms may be rationalized in terms of bent bonds as previously applied[36] to a similar triangular cobalt carbonyl complex, $Co_3(CO)_9CCH_3$, containing a triply bridging aliphatic carbon atom.

Within experimental error the crystallographically independent cyclopentadienyl ring in $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ is normal to the plane of three cobalt atoms but is tilted approximately 3° from the plane containing the cobalt atom to which it is bonded and the carbonyl and oxo ligands. This slight tilt may be attributed to the molecular packing in the crystal. Nevertheless, the cobalt–(cyclopentadienyl carbon) distances of range 2.05–2.09 Å are not significantly different from the average value of 2.07 Å.

If one considers the smaller covalent radius of oxygen (0.74 Å compared to 1.04 Å for sulfur,)[37] then the Co–O bond length of 2.02 Å is not unexpected when compared with similarly observed triply bridging sulfur to metal distances, *e.g.*, 2.17 Å in $Ni_3(\pi\text{-}C_5H_5)_3S_2$,[34] 2.14 Å in $Co_3(CO)_9S$[38] and $[Co_3(CO)_7S]_2S_2$,[39] and 2.16 Å in $FeCo_2(CO)_9S$[40] and $Co_6(CO)_{11}(S)(SC_2H_5)_4$.[41] This Co–O bond length also falls within the ranges of Co–O bond lengths of 1.99–2.13 Å observed in the compounds $Co_3[(C_2H_5O)_2P(O)CHC(O)CH_3]_6$,[42] $[Co(AcAc)_2]_4$,[43] and $[Co(AcAc)_2]_3H_2O$;[44] in the first complex the oxygen atom is coordinated to two cobalt atoms and a phosphorus atom, while in the latter two it is coordinated to a carbon and two cobalt atoms.

The observed triply bridging Co–C(carbonyl) distance of 1.78 Å is shorter than that observed in similar complexes, *e.g.*, 1.93 Å in both $Ni_3(\pi\text{-}C_5H_5)(CO)_2$ and $Ni_2Co(\pi\text{-}C_5H_5)_3(CO)_2$. This shorter (and relatively unreliable) distance presumably is a consequence primarily of the crystalline disorder which results in only a partial resolution of the superimposed carbonyl and oxygen atoms.

The cobalt–cobalt bonding distance of 2.365 ± 0.004 Å is significantly shorter than any distance previously observed for polynuclear cobalt carbonyl complexes (*i.e.*, an extensive compilation of such Co–Co bonding distances is given in ref 36) but is not significantly different from the value of 2.367 Å observed in the nitrogen-bridging cobalt cyclopentadienyl dimer, $Co_2(\pi\text{-}C_5H_5)_2\{(t\text{-}C_4H_9N)_2CO\}$.[26] The variation in electron-pair metal–metal bonding distances in ligand-bridged complexes has been shown to depend primarily on both the size and effective electronegativity of the bridging atoms.[45,46] Of particular interest is a comparison of the metal–metal bond length in $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ with those found in the related triangular metal cyclopentadienyl complexes $Ni_3(\pi\text{-}C_5H_5)_3S_2$ (Ni–Ni, 2.80 Å),[34] $Ni_3(\pi\text{-}C_5H_5)_3(CO)_2$ (Ni–Ni, 2.389 Å),[9,20] and $Ni_2Co(\pi\text{-}C_5H_5)_3(CO)_2$ (average M–M length, 2.358 Å).[20] The close similarity in the metal bond lengths of the electronically equivalent $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ and $Ni_2Co(\pi\text{-}C_5H_5)_3(CO)_2$ complexes in contrast to the longer metal–metal distances in the other two trimetal cluster complexes is expected in light of the MO bonding schemes put forward recently for this kind of metal atom cluster system.[20,34,47]

Presumably the $Co_3(\pi\text{-}C_5H_5)_3(CO)(S)$ and $Co_3(\pi\text{-}C_5H_5)_3S_2$ complexes[26] will be found to have structures very similar to $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ and $Ni_3(\pi\text{-}C_5H_5)_3S_2$. In the case of $Co_3(\pi\text{-}C_5H_5)_3S_2$ (with three fewer valence electrons than found in $Ni_3(\pi\text{-}C_5H_5)_3S_2$), the cobalt–cobalt distance is predicted from MO considerations to be considerably shorter (~2.55 Å) than the 2.80-Å distance in $Ni_3(\pi\text{-}C_5H_5)_3S_2$. Of obvious interest is whether analogous complexes of the types $Ni_3(\pi\text{-}C_5H_5)_3(CO)(L)$, $Ni_2Co(\pi\text{-}C_5H_5)_3(CO)(L)$, $Ni_2Co$-

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(35) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 960, p 260.

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$(\pi\text{-}C_5H_5)_3(L)_2$, and $M_3(\pi\text{-}C_5H_5)_3(O)_2$ (where L represents S, O, or other suitable ligands and M designates Ni or Co) can be isolated. Further preparative work is in progress along this line in order to extend the structural and bonding principles recently proposed[20,34,47] for these metal atom clusters.

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# Nonbridging Ligand Effects on the Rate of the Vanadium(II) Reduction of Some Cobalt(III) Complexes[1]

**Peter R. Guenther and R. G. Linck**

*Contribution from the Department of Chemistry, Revelle College, University of California, San Diego, La Jolla, California 92037.*

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**Abstract:** The rates of reduction of several Co(III) complexes by V(II) have been measured at 25° in a medium of unit ionic strength. The Co(III) complexes all contain a $Cl^-$ in the first coordination sphere, but the other ligands are varied. This variation leads to measured second-order rate constants between 2 and about 500 $M^{-1}$ sec$^{-1}$. These rate constants correlate well with the previously reported data on the Fe(II) reduction of the same complexes. What the implications of these linear free energy relationships are is discussed. The mechanism of the fastest of the V(II) reductions must be outer sphere; the mechanism of the slower reactions may be outer sphere also.

Those studying oxidation–reduction reactions of metal ions have always maintained an interest in the reduction of Co(III) complexes—complexes which are inert in the oxidized form but labile in the reduced form. The inertness of these complexes allowed one to vary the bridging group—to change its chemical nature significantly—and hence investigate features of the reactions that depended on the nature of this bridging group.[2] However, the complexity of the functions that a bridging group performs have made interpretation of these features difficult. Recently, renewed interest in the reduction of Co(III) complexes with simple bridging groups has arisen.[3] This interest centers around the effect of a change of nonbridging ligands[4–6] on the rate of reduction of a Co(III) complex. Since the variation in the molecule is at a site removed from the bridging ligand, it might be expected that the effect of nonbridging ligands on the rate would be more easily interpreted than those of bridging ligands.

From the data that have been accumulated on nonbridging ligand effects,[4–8] it is beginning to appear that this presumption might be true. Early evaluations of similarities in relative rates[4a] have recently been extended to encompass linear free energy relationships.[5b,6] Evidence for these relationships is, thus far, relatively fragmentary. In order to extend the number of systems studied and hence to establish that linear free energy relationships are generally to be found, we have investigated the rate of reduction of several Co(III) complexes by V(II).

While this work was in progress, Price and Taube published data that suggested to them that several reductions of Co(III) complexes by V(II) were limited in rate by the rate of water substitution on the V(II) center.[9] More recently, Sutin[10] has summarized the results on a wider variety of V(II) reductions. These two studies establish (1) that, unambiguously, several V(II) reductions proceed by the inner-sphere mechanism and (2) that the upper limit on an inner-sphere reaction of V(II) is about 40 $M^{-1}$ sec$^{-1}$. However, neither of these studies[9,10] establishes the mechanism of the V(II) reduction of $Co(NH_3)_5Cl^{2+}$, a mechanism that has been the subject of much discussion in the literature.[2a,11–13] In addition to our main purpose,

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(1) This work is taken, in part, from the M.S. dissertation of P. G., University of California, San Diego, 1968.

(2) For recent reviews, see (a) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966); (b) A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, **10**, 153 (1967).

(3) We shall use the term "bridging ligand" in the broadest possible sense: that ligand which does serve, or most probably would serve, as the bridging ligand if the reaction proceeds by an inner-sphere path. In practice, for outer-sphere reactions, it is the ligand in the coordination sphere that is not changed in the series of compounds under investigation; for inner-sphere reactions, it is important for the success of linear free energy relationships that this ligand is the bridging ligand.

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