quencies for comparison of CO bond strengths. A similar conclusion has been reached by Bower and Stiddard[35] from a study of substituted hexacarbonyls.

Bending Force Constants.—The constant F_β, for MCO bending, is about the same (0.47 mdyn Å/radian^2) for all three hexacarbonyls. It is significantly greater than the value for nickel carbonyl (0.31). This may arise from the greater M–CO π bonding leading to a more rigid linear MCO group for the hexacarbonyls. The CMC bending constant, F_α, is very much greater for the hexacarbonyls than for $Ni(CO)_4$ (compare 0.5–0.6 mdyn Å/radian^2 with 0.2–0.3). This must arise either from carbon–carbon interaction (which is, of course, greater for the smaller CMC angle) or from more rigidly directional valence orbitals for the hexacarbonyls, or both. It will be interesting to compare these results with the 90 and 120° CMC bending constants of $Fe(CO)_5$.

At the present time the implications of the bend–bend interactions are not obvious. The values are rather small and it will be much more appropriate to relate the interaction displacement coordinates to the bond structure.

Conclusion

The vibrational spectra of the species $M(^{12}C^{16}O)_6$, $M(^{13}C^{16}O)_6$, and $M(^{12}C^{18}O)_6$ have been observed and valence force constants have been calculated therefrom, using a general quadratic valence force field. Most of the interaction constants (see Table XIX) are appropriate for transfer to other metal carbonyls having similarly oriented MCO groups, but for which sufficient information for an independent normal-coordinate calculation is lacking. The CO,C′O′ interactions are shown to be consistent with the oscillating dipole model discussed by Haas and Sheline,[33] without a significant contribution from changes in π bonding.

The results are compared with those for nickel carbonyl.[8] The values of the primary force constants, as well as the interaction constants, form a consistent picture. The metal–ligand π bonding is apparently greater for the hexacarbonyls, in agreement with molecular orbital studies.[31] The W–C σ bonding is significantly stronger than for Cr–C and Mo–C. The results lend encouragement for the establishing of order in the relations of force constants to bonding and structure for the metal carbonyls.

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Raman Frequencies and Metal–Metal Force Constants for $M_2(CO)_{10}$ Species[1]

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Raman spectra are reported for $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $MnRe(CO)_{10}$. A simple normal-coordinate analysis was applied to the low-frequency vibrations of the transition metal decacarbonyls in order to estimate metal–metal stretching force constants. The following values (in mdyn/Å) were obtained: $f_{Mn-Mn} = 0.59$, $f_{Tc-Tc} = 0.72$, $f_{Re-Re} = 0.82$, $f_{Mn-Re} = 0.81$. The force constances correlate satisfactorily with bond dissociation energies obtained from electron impact measurements. The present results are discussed together with previous analyses of $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Ir_4(CO)_{12}$. For the polynuclear carbonyls, metal–metal force constants increase with increasing atomic number within a given row or period, in accord with the expectation based on chemical stabilities, mass spectral fragmentation patterns, and internuclear distances. Metal–metal force constants calculated with neglect of the carbonyl ligands are not seriously in error and are quite satisfactory for the third transition row.

Introduction

The transition metal carbonyls offer a rich variety of polynuclear structures for the study of metal-to-metal bonding. Much interest attaches to the simplest representatives, the dinuclear decacarbonyls, $M_2(CO)_{10}$ (M = Mn, Tc, Re), in which two square-pyramidal $M(CO)_5$ groups are joined in a staggered orientation by an M–M bond[2–4] (Figure 1). Assignments of metal–metal stretching frequencies in Raman spectra have been suggested for $Re_2(CO)_{10}$,[5–7] $Mn_2(CO)_{10}$,[8,9] $MnRe(CO)_{10}$,[8] and $Tc_2(CO)_{10}$.[10] We present here a study of the low-frequency Raman spectra of these molecules,

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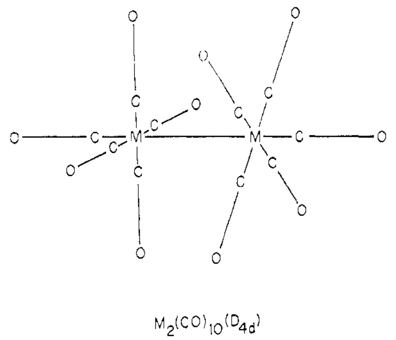

Figure 1.—Idealized structure for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.

together with normal-coordinate calculations of the metal–metal stretching force constants.

Spectra and Assignments

Raman frequencies observed for crystalline $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $MnRe(CO)_{10}$ are listed in Table I. The data are in general agreement with previous results[5–9] except for certain discrepancies in the low-frequency region (*vide infra*). This is the first report of the full Raman spectrum for $MnRe(CO)_{10}$.

Table I

Observed Raman Frequencies[a] (cm^{-1})

$Mn_2(CO)_{10}$	$Re_2(CO)_{10}$	$MnRe(CO)_{10}$
2115 m	2127 m	2126 m
2023 m	2027 m	2117 vw
2014 m	2018 m	2038 w
1991 s	1989 m	2025 vw
1982 m	1978 s	2009 m
1971 w	616 w	2003 m
674 w	595 w	1986 s
555 vw	536 w	1965 vw
480 w	476 s	588 vw
464 w	459 s	562 w
412 s	452 w, sh	540 w
160 vs	394 390 } s	478 m
133 m		453 m
116 w	122 s	413 s
95 m	109 m, sh	391 m
69 w	99 w, sh	163 w, sh
38 m	80 m	157 m
	65 m	140 } m, br
	32 m	126
		111
		95
		80
		68
		36 m

[a] Symbols: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder.

Below 200 cm^{-1}, Raman bands are expected for vibrations involving metal–metal stretching and metal–carbon deformation. The Raman-active representations spanned by symmetrically complete sets of these coordinates are given in Table II for $M_2(CO)_{10}$ (D_{4d}) and $MM'(CO)_{10}$ (C_{4v}). Seven Raman-active fundamentals, from metal–metal stretching (one) and metal–carbon deformation (six), are predicted for $M_2(CO)_{10}$ (D_{4d}).

Table II

Symmetries of Low-Frequency Raman-Active Vibrations

$M_2(CO)_{10}$ (D_{4d})

$$\Gamma\nu_{M-M} = A_1$$
$$\Gamma^{rad}_{\delta C-M-C^a} = E_2 + E_3$$
$$\Gamma^{ax}_{\delta C-M-C^{a,b}} = A_1 + E_2 + E_3$$
$$\Gamma_{\delta M-M-C^b} = A_1 + E_2 + E_3$$

$MM'(CO)_{10}$ (C_{4v})

$$\Gamma\nu_{M-M} = A_1$$
$$\Gamma^{rad}_{\delta C-M-C} = B_1 + B_2 + 2\,E$$
$$\Gamma^{ax^c}_{\delta C-M-C} = 2\,A_1 + B_1 + B_2 + 2\,E$$
$$\Gamma_{\delta M-M-C^c} = 2\,A_1 + B_1 + B_2 + 2\,E$$

[a] Abbreviations: rad, both M–C bonds are radial; ax, one M–C bond is axial. [b] Contains $A_1 + E_2$ redundancies. [c] Contains $2\,A_1 + B_1 + B_2$ redundancies.

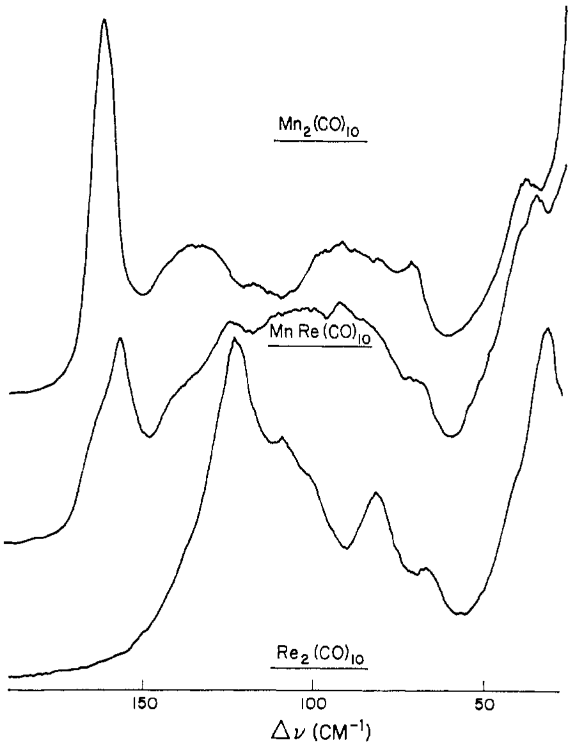

Figure 2.—Low-frequency Raman spectra of polycrystalline $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$, ahd $Re_2(CO)_{10}$. Conditions: 6328 Å He–Ne laser excitation; slit width 4 cm^{-1}; time constant 10 sec; scan rate 12 cm^{-1}/min.

For $MM'(CO)_{10}$ the number of metal–carbon deformation modes increases to 14.

The low-frequency spectra are shown in Figure 2. For $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, six bands can be observed, while the $MnRe(CO)_{10}$ spectrum is too complex to allow a reliable count. In each case a sharp, strong band is observed, at 160, 157, and 122 cm^{-1} for $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$, and $Re_2(CO)_{10}$, which may readily be assigned to metal–metal stretching. $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ solution spectra (CCl_4) show this band to be polarized, as required. The remainder of the $Re_2(CO)_{10}$ spectrum is nearly identical in appearance with that of $Mn_2(CO)_{10}$ but shifted somewhat to lower frequencies. The remainder of the $MnRe(CO)_{10}$ spectrum is essentially a superposition of the $Mn_2(CO)_{10}$ and

$Re_2(CO)_{10}$ spectra. The site symmetry in the $M_2(CO)_{10}$ crystals is only C_2 and the expected splittings in E-type deformation modes may be reflected in the breadth of some of the observed bands.

These metal–metal assignments are in agreement with those made previously for $Mn_2(CO)_{10}$ by Gager, Lewis, and Ware[8] and by Adams and Squire[9] and for $Re_2(CO)_{10}$ by Cotton and Wing[5] and Lewis, *et al.*[6] Hyams, Jones, and Lippincott,[7] however, preferred to assign the 122-cm^{-1} $Re_2(CO)_{10}$ band to the symmetric metal–carbon deformation, since in $Re(CO)_5I$ they found this mode at 130 cm^{-1}. They observed another polarized $Re_2(CO)_{10}$ emission in $CHCl_3$ at 106 cm^{-1} and assigned it to ν_{Re-Re}. We confirmed the existence of a band at this frequency in CCl_4 solution but were unable to detect any polarization for it. While a polarized (A_1) deformation mode is expected, its intensity should be quite low, arising primarily from mixing with the M–M stretching mode. In the Wolkenstein theory of Raman intensities[11,12] bond angle deformations do not contribute to the isotropic part of the molecular polarizability derivative. For valence angles of 90°, the anisotropic contribution from deformation is likewise predicted to be zero. Furthermore, the interaction between the two A_1 modes makes a separation as low as 20 cm^{-1} highly unlikely.

Our normal-coordinate analysis (see below) places the A_1 bending mode at 57 cm^{-1}. It is not observed and indeed mixing with the Re–Re stretch is slight, nor is the A_1 deformation of $Mn_2(CO)_{10}$ (calculated at 56 cm^{-1}) observed. Examination of the eigenvectors for these vibrations indicates their intensities should be only about 5% of the respective metal–metal stretching bands. It seems reasonable to assume, therefore, that the A_1 C–M–C deformation modes are too weak to be observed and are the missing bands in the low-frequency $M_2(CO)_{10}$ Raman spectra.

Gager, Lewis, and Ware[8] reported $\nu_{M-M'}$ for $MnRe(CO)_{10}$ at 185 cm^{-1}, but we found no Raman emission there. This frequency does coincide, however, with a fairly strong neon discharge line, which can interfere as stray light during He–Ne laser excitation. Gager, *et al.*, also observed a band at 157 cm^{-1}, which we assign to ν_{Mn-Re}, but they attributed it to $Mn_2(CO)_{10}$ impurity. The frequency shift from the sharp 160-cm^{-1} band of $Mn_2(CO)_{10}$ is significant, however. The $MnRe(CO)_{10}$ spectrum in Figure 2 shows a 160-cm^{-1} shoulder on the 157-cm^{-1} band, which may be due to $Mn_2(CO)_{10}$. Careful examination of the Raman and infrared spectra of our $MnRe(CO)_{10}$ sample in the carbonyl region ruled out a substantial $Mn_2(CO)_{10}$ content.

The observed $M_2(CO)_{10}$ deformation modes are in general agreement with published frequencies[7,9] except for the 38- and 32-cm^{-1} bands of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, respectively, which have not previously been reported. We have observed similar very low-frequency bands for the polynuclear carbonyls $Ir_4(CO)_{12}$,[13] $Os_3(CO)_{10}$,[14] and $Ru_3(CO)_{12}$.[14] They were assigned with the aid of normal-coordinate analyses to M–M–C bending modes. Assignment to external modes was rejected because the frequencies are not sensitive to changes in molecular weight or moments of inertia of the heavy metal carbonyls.

The Raman spectrum of $Tc_2(CO)_{10}$ has very recently been obtained by Levenson and Gray.[10] A strong band at 148 cm^{-1} in cyclohexane was assigned to ν_{Tc-Tc}. The M–C deformation modes were not resolved.

Normal-Coordinate Analysis

An approximate normal-coordinate analysis was carried out in order to assign the low-frequency modes and to obtain estimates of the metal–metal stretching force constants. The *G* matrices were calculated by the method of Wilson, *et al.*,[15] using Schachtschneider's program GMAT.[16] Molecular parameters, given in Figure 1, were average values taken from the X-ray structure determinations.[2,3] Since carbonyl parameters for $Re_2(CO)_{10}$ were not determined accurately,[2] the parameters for $Tc_2(CO)_{10}$[4] were used instead. The small deviations from mutual orthogonality of the axial and radial carbonyls were ignored. A valence force field was used to construct the *F* matrices. Both *G* and *F* matrices were factored using symmetry coordinates by standard group theoretical techniques. The internal coordinates (Table II) contain redundancies, which were removed as a first step in solving the secular equations with Schachtschneider's least-squares program FPERT.[16]

The matrices were set up for calculation of all the fundamental frequencies, but only those below 200 cm^{-1} were used to obtain a least-squares fit to the observed Raman spectrum. Force constants for C–O and M–C stretching and M–C–O bending were estimated from the literature and held fixed. Previous experience has shown that small changes in these values have no significant effect upon the low frequencies.[14] The initial values of f_{M-M} were estimated from the metal–metal frequencies using the metal diatom approximation. The three valence M–C bending force constants f^{rad}_{C-M-C}, f^{ax}_{C-M-C}, and f_{M-M-C} were expected to fall in the range 0.1–0.6 mdyn/Å, with $f^{rad}_{C-M-C} \geqq f^{ax}_{C-M-C} > f_{M-M-C}$. Initial calculations with various values of the bending constants within the expected range showed a distinct ordering of the calculated frequencies. They could be assigned on a one to one basis to the experimental frequencies for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ assuming that the A_1 bending modes were unobserved. Refinement of the force constants then proceeded smoothly to a satisfactory

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TABLE III

NORMAL-COORDINATE CALCULATIONS

Raman freq, cm^{-1}		
Obsd	Calcd	V_{M-M}[a]
	$Mn_2(CO)_{10}$	
160	160.0 (A_1)	71.4
133	129.6 (E_2)	...
116	121.0 (E_3)	...
95	95.1 (E_3)	...
69	62.4 (E_2)	...
...	56.1 (A_1)	21.7
38	40.7 (E_3)	...
	$Re_2(CO)_{10}$	
122	122.0 (A_1)	77.3
109	108.3 (E_2)	...
99	99.8 (E_3)	...
80	86.3 (E_3)	...
65	62.3 (E_2)	...
...	56.8 (A_1)	21.2
32	32.3 (E_3)	...
	$MnRe(CO)_{10}$	
157	157.0 (A_1)	74.6
	$Tc_2(CO)_{10}$	
148	148.0 (A_1)	73.3

[a] Represents percentage contribution to the potential energy from the force constant f_{M-M}.

TABLE IV

ADJUSTED FORCE CONSTANTS

Metal-metal stretching[a]		Metal-carbon deformation[b]		
			δ_{Mn}	δ_{Re}
f_{Mn-Mn}	0.59	f^{eq}_{C-M-C}	0.57	0.41
f_{Mn-Re}	0.81	f^{ax}_{C-M-C}	0.34	0.40
f_{Re-Re}	0.82	f_{M-M-C}	0.10	0.09
f_{Tc-Tc}	0.72			

[a] Units: mdyn/Å. [b] Units: mdyn Å.

least-squares fit of the observed frequencies, as shown in Table III. The adjusted force constants are given in Table IV.

For $MnRe(CO)_{10}$ no least-squares fit was possible because of the severe overlap of the bending modes. Instead the bending constants for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were transferred without adjustment, and f_{M-M} was varied to calculate ν_{Mn-Re} exactly. A similar calculation, using averages of the $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ bending constants, was performed for $Tc_2(CO)_{10}$ to fit the ν_{Tc-Tc} observed by Levenson and Gray.[10]

Discussion

The normal-coordinate analysis presented here is a highly approximate one. Its limited purpose is to obtain a basis for a reasonable assignment of the spectra and approximate metal-metal force constants. To this end, a minimum number of valence force constants have been chosen to provide a satisfactory account of the Raman spectra and only the region below 200 cm^{-1} has been reproduced in detail. We fully recognize that some interaction constants may well be nonzero, but unfortunately there is little basis for evaluating them. Nevertheless, we feel that the resulting f_{M-M} are unlikely to be seriously in error, although we make no attempt to justify the remainder of the force field in detail.

It is instructive to compare the diatom approximation, neglecting the carbonyl ligands completely, with the normal-coordinate analysis result. The two sets of force constants are given in Table V. When the metal atoms are as light as manganese mixing in of other coordinates affects the calculation significantly and f_{M-M} from the diatom approximation is 30% low. For the much heavier rhenium analog, however, the error is negligible. The discrepancies for the mixed complex and for $Tc_2(CO)_{10}$ are intermediate. Metal-metal force constants have previously been calculated on the diatom approximation but with the full mass of $M(CO)_5$ for the vibrating unit.[8] The resulting values are too high by 100% or more. Inclusion of the carbonyl ligands in the "effective" mass of the metal atoms vastly overcorrects for the neglect of interaction with ligand modes. Similar results were obtained for the triangular clusters $Ru_3(CO)_{12}$[14] and $Os_3(CO)_{12}$[14] (Table V). Approximate metal-metal force constants for these species can be simply calculated by neglecting the ligands and using only the A_1 frequency: $f_{M-M}' = {}^1/_2 m_M \lambda^{A_1}_{M-M}$ mdyn/Å, where m_M is the mass of the metal atom and $\lambda = 0.5885(\nu(\text{cm}^{-1})/1000)^2$. This procedure gives the correct value for the heavy osmium cluster and introduces an error of 17% for the lighter ruthenium species. Again inclusion of the carbonyl ligands in the metal "effective" masses grossly overestimates both force constants and also inverts their order.[17] The case of the tetrahedral cluster $Ir_4(CO)_{12}$[13] (Table V) is a little more complicated since substantial M-M stretch-stretch interaction constants are required to fit the observed frequencies. Consequently f_{M-M} is considerably higher than might be expected from a simple model. However the symmetry A_1

TABLE V

METAL-METAL FORCE CONSTANTS FOR POLYNUCLEAR CARBONYLS

	f_{M-M}, mdyn/Å			
Molecule	NCA[a]	NOL[b]	M-M, Å	D_{M-M},[c] eV
$Mn_2(CO)_{10}$	0.59	0.41	2.92[d]	0.96
$Tc_2(CO)_{10}$	0.72	0.63	3.04[e]	
$Re_2(CO)_{10}$	0.82	0.82	3.02[f]	2.22
$MnRe(CO)_{10}$	0.81	0.62		2.67
$Ru_3(CO)_{12}$	0.82[g]	0.68	2.85[i]	
$Os_3(CO)_{12}$	0.91[g]	0.93	2.89[j]	
$Ir_4(CO)_{12}$	1.69[h] (F_{A_1} = 1.30)	1.22	2.68[k]	

[a] Normal-coordinate analysis result. [b] Simple valence force estimate with neglect of ligands. For the tri- and tetranuclear species the estimate is based on the A_1 frequency. [c] H. J. Svec and G. A. Junk, *J. Am. Chem. Soc.*, **89**, 2836 (1967). [d] See ref 3. [e] See ref 4. [f] See ref 2. [g] See ref 14. [h] See ref 13. [i] R. Mason and A. I. M. Rae, *J. Chem. Soc., A*, 778 (1968). [j] E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962). [k] G. R. Wilkes, *Dissertation Abstr.*, **26**, 5029 (1966).

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M–M force constant is quite close to the approximate constant calculated with neglect of ligands from the A_1 frequency: $f_{M-M} = {}^1/_4 m_M \lambda^{A_1}_{M-M}$. In general it appears that neglect of carbonyl ligands produces negligible errors in the calculation of metal–metal force constants for third-row transition elements, and even in the first row the error does not exceed 30%. Such calculations are quite simple and, in the absence of normal-coordinate analyses, may be expected to yield useful estimates. When heavier ligands, such as halides, are present, mixing is apt to be severe[18] and their neglect would lead to more serious errors.

Examination of the metal–metal force constants for the seven polynuclear carbonyls listed in Table V reveals some notable trends. Within a given row or period f_{M-M} values increase with increasing atomic number, in accord with expectation based on chemical stabilities and mass spectral fragmentation patterns.[19–21] Moreover the force constants for the dinuclear carbonyls correlate satisfactorily with M–M bond dissociation energies estimated from electron impact measurements.[22] In particular the exceptional stability of the Mn–Re bond is revealed in both quantities, although it is more pronounced in the D_0 estimates. For the third-row transition carbonyls the increase of f_{M-M} from $Re_2(CO)_{10}$ to $Os_3(CO)_{12}$ to $Ir_4(CO)_{12}$ correlates with decreasing metal–metal bond length. However force constants for different geometries are not strictly comparable because the force fields have different forms. Indeed the very large increase from f_{Os-Os} to f_{Ir-Ir} is out of proportion to the decrease in bond length and no doubt reflects the greater complexity of the $Ir_4(CO)_{12}$ force field. The A_1 symmetry force constant for $Ir_4(CO)_{12}$, 1.30 mdyn/Å, seems to provide a more reasonable basis for comparison.

Experimental Section

$Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were obtained from Alfa Inorganics, Inc., and were used as received. $MnRe(CO)_{10}$ was prepared according to Flitcroft, *et al.*,[23] and purified by sublimation. The purity of the compounds was verified by infrared spectroscopy in the carbonyl region using a Beckman IR12.

Raman spectra were obtained with a spectrometer[24] equipped with an He–Ne laser source at a nominal power of 50 mW (6328 Å). The samples were held in a 1-mm thin-walled X-ray capillary placed perpendicular to the laser beam. Scattered light was collected at 90°.

Acknowledgment.—We are indebted to Professor Harry B. Gray and Dr. Robert Levenson for communicating their Raman results on $Tc_2(CO)_{10}$ in advance of publication.

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The Crystal and Molecular Structure of *trans*-Dichlorotetrakis(thiourea)cobalt(II)

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The crystal structure of *trans*-dichlorotetrakis(thiourea)cobalt(II), $Co[SC(NH_2)_2]_4Cl_2$, has been determined by three-dimensional X-ray diffraction techniques from 885 reflections measured with an automatic diffractometer. The compound crystallizes in the tetragonal space group $P4_2/n$ with $a = b = 13.508 \pm 0.007$ Å, $c = 9.106 \pm 0.005$ Å, $D_m = 1.72$ g/cm^3, and $D_c = 1.72$ g/cm^3 for $Z = 4$. The structure, including hydrogen atoms, was refined by least-squares methods to a conventional R of 0.045. The structure consists of discrete molecules interconnected with hydrogen bonds. However, it is not isostructural with *trans*-$Ni[SC(NH_2)_2]_4Cl_2$ as previously reported. The cobalt atom is located on a center of symmetry and is octahedrally coordinated to four sulfur and two chlorine atoms. The two independent Co–S distances are 2.502 and 2.553 Å, both ±0.006 Å; the Co–Cl distance is 2.469 ± 0.002 Å. The S–C (1.712 and 1.730 Å, both ±0.013 Å) and C–N (average 1.311 Å with individual esd's of ±0.016 Å) bond lengths do not differ significantly from each other nor from values reported for free thiourea and other thiourea complexes. The thiourea groups, including hydrogens, are planar well within experimental error. $M^{II}[SC(NH_2)_2]_4Cl_2$ is an isomorphous series when M is Co, Fe, Mn, and Cd.

Introduction

As a part of the systematic investigation of metal–sulfur bonds in thiourea complexes, we have investigated the crystal structure of *trans*-dichlorotetrakis(thiourea)cobalt(II), $Co(tu)_4Cl_2$ [tu = $SC(NH_2)_2$]. As a ligand thiourea has several modes of binding to a metal atom, and thiourea complexes of the transition metals have exhibited some interesting and unusual properties.[2] $Co(tu)_4Cl_2$, as well as the analogous iron, manganese,

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