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Crystal Structure of $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$ and $Cd_3[Co(CN)_6]_2 \cdot 12H_2O$ by Neutron and X-Ray Diffraction[1]

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Received July 8, 1977

AIC70499V

The crystal structure of $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$ has been determined by neutron and x-ray diffraction methods and that of $Cd_3[Co(CN)_6]_2 \cdot 12H_2O$ by the latter method. In both cases, the space group is *Fm3m* with lattice constants of 10.436 (3) and 10.600(3) Å, respectively. The structure is disordered and contains 1.33 formula weights per unit cell. The only atom that is not disordered is the manganese or cadmium atom. The structure is held together by cyanide links between the cobalt atom and manganese or cadmium atom. Eight of the water molecules (24e in the unit cell) are coordinated to the manganese or cadmium atom, and the other eight water molecules are of two types. The first type (2.66 molecules) in the 8c ($^1/_4$, $^1/_4$, $^1/_4$) position is contained in holes and not hydrogen bonded to any other water molecules. The second type (5.33 molecules) in position 32f (0.16, 0.16, 0.16) is hydrogen bonded to the coordinated water molecules. The final R values are 8.8, 7.2, and 4.3%, and R_w values are 7.4, 8.8, and 5.5%, respectively, for Mn (neutron), Mn (x ray), and Cd (x ray). Dehydration studies were also made on single crystals of $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$.

Introduction

In the past, the structure of $M^{II}{}_3[Co(CN)_6]_2 \cdot 12H_2O$ where M^{II} = Mn or Cd has been described in terms of a structural model developed for Prussian blue by Weiser, Milligan, and Bates.[3] Owing to the high insolubility of the transition metal–cyanide complexes, these early studies were performed on powders. Ludi[4–6] was the first person to obtain single crystals of these salts. On the basis of the single-crystal studies performed by Ludi et al.,[4–6] a new model was proposed in which all atoms in the structure, except the divalent metal, are disordered. The model was not refined anisotropically and contained a divalent metal with a distorted coordination octahedron of two water molecules and four cyanides. The distortion of the octahedron is reportedly caused by water molecules hydrogen bonded to the coordinated water molecules. Our studies were initiated because (a) the model proposed by Ludi[4–6] seemed somewhat inadequate and (b) we have great interest in the semipermeable membrane properties of the Prussian blue analogues.

Experimental Section

Crystals were grown by slow diffusion of solutions of $MnCl_2$ (or $CdCl_2$) and $H_3Co(CN)_6$. The crystals of $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$ are pale yellow, and the Cd salt is colorless. Cube-shaped crystals 0.1 mm on an edge were mounted on a Syntex $P\bar{1}$ computer-controlled, four-circle diffractometer equipped with a graphite incident beam monochromator. Least-squares refinement of 15 centered reflections produced the orientation matrix for data collection and gave cell constants of 10.436 (3) and 10.600 (3) Å for Mn and Cd salts, respectively. Data were collected in the range of $0 < 2\theta < 100°$ using Mo Kα, λ 0.71069 Å. The θ–2θ scan technique with a variable scan rate from 2.0 to 24°/min was used. Additional details about the method of data collection have been described previously.[7] Three reflections were chosen as standards and monitored every 50 reflections to check stability. Sets of reflections, 160 for the Mn salt and 150 for Cd salt, with $I > 3\sigma$ were used in least-squares refinement. Single crystals of the Mn salt were also sealed in Mark capillaries and dehydrated. Data were obtained on a half-hydrated and a totally dehydrated crystal in the same manner as above. The lattice constant for the partially dehydrated crystal is 10.330 (6) Å and for the totally dehydrated crystal, 10.22 (1) Å. The data sets were all corrected for Lorentz and polarization effects. An absorption correction employing crystal shape was also applied.[8]

The neutron data was collected on a $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$ crystal that was approximately 1.5 mm on an edge. The crystal was mounted on a glass capillary and placed on a computer-controlled four-circle diffractometer at the Brookhaven National Laboratory high flux beam reactor such that the [001] direction was nearly parallel to the ϕ axis. A wavelength of 1.0188 Å was selected by means of a Ge (311) crystal monochromator. Intensity data were collected at 24 °C using a θ:2θ step scan varying from 1.80 to 3.00° 2θ out to a maximum of 2θ = 90°. One entire octant of data was collected. Two standard reflections (400 and −2,2,2) were checked after every 30 intensity measurements throughout the course of the data collection, and they showed no systematic variation in intensity.

The data were corrected for Lorentz effects, and an analytical absorption correction was made [μ(neutrons) = 1.218 cm^{-1}]. The correction factor ranged from 1.068 to 1.121. The data from the entire octant were averaged, with a residual error of 4.1%. The residual is defined as $R' = \sum|F_o - F_{av}|/\sum|F_o|$. This resulted in 72 unique reflections for refinement.

Structural Refinement

The positional parameters proposed by Ludi[4] were used as a starting model for the metal, carbon, and nitrogen atoms in the neutron refinement. The carbon and nitrogen temperature factors were initially set at the values[9] found in $Cs_2LiCo(CN)_6$. A Fourier synthesis phased with these atoms yielded possible positions for the water molecules including hydrogen atoms. Several cycles of full-matrix refinement[11] yielded a final R of 8.8% and R_w of 7.4%, where R and R_w are

$$R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$$

and

$$R_w = \Sigma w ||F_o| - |F_c||/\Sigma w |F_o|$$

where $w = 1/\sigma^2$. There were high correlations between the temperature and positional parameters for the water molecules in the 32f (0.16, 0.16, 0.16) and 8c ($^1/_4$, $^1/_4$, $^1/_4$) positions; therefore, these parameters could not be refined simultaneously. The hydrogens were located in a Fourier synthesis phased by the metal, carbon, nitrogen, and oxygen atoms. The parameters for the hydrogen atoms were not refined in the least-squares refinement, owing mainly to their low occupancies.

The x-ray refinement of $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$ was carried out employing the positions derived from the neutron refinement for the heavy atoms. A difference Fourier synthesis failed to reveal hydrogen positions so they were not included in the refinement. The final R and R_w for the x-ray data were 7.2 and 8.8%, respectively. A secondary extinction correction was also applied in this refinement.[9] The value of the secondary extinction parameter was 2.0 (1) × 10^{-6}.

The least-squares refinement of $Cd_3[Co(CN)_6]_2 \cdot 12H_2O$ was carried out employing the thermal parameters derived from the neutron data on the Mn salt. All positional parameters were refined. The coordinated water molecules are sufficiently displaced from the nitrogen such that the positional parameters refined completely. The final refinements yielded an R value of 4.3% and R_w of 5.5%. The scattering factors for the x rays were obtained from Cromer and Mann.[12] Anomalous dispersion corrections both real and imaginary were made for all atoms.[13] The neutron scattering lengths used in the neutron refinement were b(Mn) = −0.36, b(Co) = 0.25, b(C) = 0.663, b(N) = 0.940, b(O) = 0.575, and b(H) = −0.372 cm (all ×10^{-12}).

Description of the Structure

The structure derived from the neutron and x-ray refinements consists of divalent metal ions linked to cobalt atoms

Table I. Positional and Thermal Parameters for $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$ (Neutron and X-Ray Refinements)

Atom	x	y	z	B, Å^2	β_{11}[a]	β_{22}	β_{33}	Occupancy
				Neutron				
Mn	0	0	0.5	2.11 (34)				1
Co	0	0	0	1.67 (60)				$^2/_3$
C	0	0	0.1804 (6)		80 (6)	80 (6)	32 (7)	$^2/_3$
N	0	0	0.2907 (9)		152 (8)	152 (8)	38 (10)	$^2/_3$
O(1)	0	0	0.2919 (62)		587 (177)	587 (177)	150 (141)	$^1/_3$
O(2)	0	0	0	7.0				$^1/_3$
O(3)	0.1611	0.1611	0.1611	7.0 (28)				$^1/_6$
O(4)	0.25	0.25	0.25	7.0 (20)				$^1/_3$
H(1)	0.1	0.1	0.225	8.0				$^1/_6$
H(2)	0.06	0.06	0.24	8.0				$^1/_6$
H(3)	0.05	0.05	0.05	8.0				$^1/_3$
H(4)	0.1	0.1	0.1	8.0				$^1/_3$
H(5)	0.1	0.225	0.225	8.0				$^1/_6$
				X-Ray				
Mn	0	0	0.5	2.11				1
Co	0	0	0	1.67				$^2/_3$
C	0	0	0.1804		80	80	32	$^2/_3$
N	0	0	0.2907		152	152	38	$^2/_3$
O(1)	0	0	0.2937 (65)		587	587	150	$^1/_3$
O(2)	0	0	0	7.0				$^1/_3$
O(3)	0.1611 (58)	0.1611 (58)	0.1611 (58)	6.9 (23)				$^1/_6$
O(4)	0.25	0.25	0.25	7.0 (20)				$^1/_3$

[a] All β's $\times 10^{-4}$.

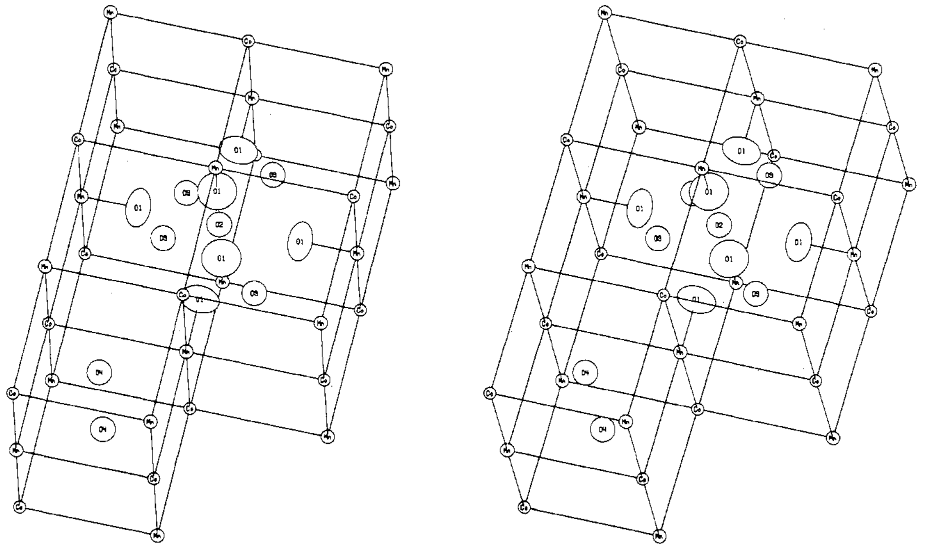

Figure 1. Representation of the disordered and ordered portions of the $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$ structure.

by cyanides. The cyanide ligands are oriented with the carbon atom toward the cobalt atom. The manganese atom is in position set 4b (0, 0, $^1/_2$) and is the only atom with a population factor of 1. The cobalt atom is in position set 4a (0, 0, 0) and has an occupancy of $^2/_3$. The cyanide ligands likewise are disordered in a manner analogous to the cobalt atom. The carbon and nitrogen atoms are in the 24e (0, 0, x) position where x = ca. 0.17 and 0.29 for carbon and nitrogen atoms, respectively. Whenever the cyanide ligands are disordered, water molecules O(1) coordinate to the manganese atom in the 24e position with x = ca. 0.29. The model proposed by Ludi[4] places this water in the 192l position at 0.01, 0.053, 0.277. In Ludi's refinement the nitrogen atom was refined isotropically; therefore, the oxygen atom in Ludi's model was only compensating for the anisotropic character of the nitrogen atom. There are eight coordinated water molecules per unit cell and three positions for uncoordinated water in the unit cell. The first two positions, O(2) and O(3), are at (0, 0, 0) when the cobalt is missing (1.33 molecules) and 32f (0.16, 0.16, 0.16) (4 molecules). The water molecules contained in the 32f set are within hydrogen bonding distance of both O(1) and O(2). The hydrogen atom positions are along lines connecting O(1), O(2), and O(3). These hydrogen atom positions are given in Table I along with the thermal and positional parameters for all the atoms in the structure. The fourth type of water molecule is in position set 8c ($^1/_4$, $^1/_4$, $^1/_4$) and is within 1.6 Å of O(3). This is the average disorder structure seen by neutron and x-ray analysis. To explain the data we propose the following model. The structure can be divided into two basic structural units, which are pictured in Figure 1. The first unit consists of a completely ordered arrangement of the metal atoms and cyanide ligands. The cube contains a water molecule located at its center. Water molecule O(4) is merely occupying space and is over 3.6 Å away from the nearest atom. This unit occurs one-third of the time in the overall structure. The second structural unit occurs when two cobalts are missing per unit cell. In this case, O(1) fills the coordination of the manganese and O(2) and O(3) set up a strong hydrogen-bonding network. This unit occurs two-thirds of the time in the structure. The figure portrays the case where only one cobalt is missing in the disordered portion of the structure for clarity's sake.

Spectroscopic data are consistent with this model. For instance the infrared spectrum has two peaks for the O–H

Table II. Bond Distances (Å) for $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$ (X Ray), $Cd_3[Co(CN)_6]_2 \cdot 12H_2O$, and $Cs_2LiCo(CN)_6$ [9,a]

Bond	$Mn_3[Co(CN)_6]_2 \cdot 12H_2O$	$Cd_3[Co(CN)_6]_2 \cdot 12H_2O$	$Cs_2LiCo(CN)_6$ [9]
Co–C	1.882 (6)	1.872 (15)	1.886 (3)
M^{II}–N	2.184 (9)	2.268 (29)	2.213 (3)
C–N	1.152 (11)	1.160 (32)	1.148 (5)
M^{II}–O(1)	2.153 (65)	2.53 (16)	
O(1)–O(2)	3.07 (6)	2.77 (16)	
O(1)–O(3)	2.75 (5)	3.30 (25)	
O(2)–O(3)	2.91 (10)	3.90 (30)	
O(3)–O(3)	2.62 (8)		

[a] The hydrogen positions were not refined due to their low occupancy. All the values for the O–H distances are estimated from Fourier peak positions.

Table III. Distances (Å) and Angles (deg) for the Hydrogen Bonding Network in $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$[a]

	Distances		
O(1)–H(2)	1.09 (8)	O(1)···H(1)	1.64 (8)
O(2)–H(3)	1.10 (8)	O(2)···H(4)	1.65 (8)
O(3)–H(4)	1.12 (9)	O(3)···H(2)	1.70 (8)
O(3)–H(1)	1.14 (9)	O(3)···H(3)	1.80 (8)
O(3)–H(5)	0.9 (8)	O(3)···H(5)	1.80 (8)
	Angles		
H(2)–O(1)–H(2)	118 (1)	O(1)–H(2)–O(3)	179 (1)
H(4)–O(3)–H(5)	111 (1)	O(1)–H(1)–O(3)	169 (1)
H(5)–O(3)–H(5)	108 (1)	O(2)–H(4)–O(3)	180
H(1)–O(3)–H(1)	110 (1)	O(2)–H(3)–O(3)	180
H(3)–O(2)–H(3)	109 (1)	O(3)–H(5)–O(3)	125 (1)

[a] The hydrogen positions were not refined due to their low occupancy. All the values for the O–H distances are estimated from Fourier peak positions.

stretching frequency (3650 and 3400 cm^{-1}). The first peak can be attributed to O(4), the water contained in holes in the structure (Figure 1). This peak is sharp compared to the second one which can be attributed to the hydrogen-bonded oxygens O(1), O(2), and O(3). The relative area of the peaks is also consistent with the amounts of each type of water. Again, evidence can be obtained from thermal gravimetric analysis with which it was found that the total amount of water was variable depending upon humidity and temperature. The variability is from 12 to 14 water molecules per formula unit, which is quite consistent with our structural model.

Experiments have shown that single crystals can be fully or partially dehydrated. The x-ray data collected on the half-dehydrated single crystal yield a lattice constant of 10.330 (6) Å, and results from a least-squares refinement indicate that the O(4) water molecule is no longer present. The other water molecules involved in the hydrogen bonding network are absent in equal amounts. This indicates that once O(2) and O(3) leave, the lattice O(1) is destabilized and can be taken off easily. The x-ray data taken on a totally dehydrated crystal yielded a lattice constant of 10.22 (1) Å. The amount of data was very limited owing to the increase in mosaic character of the peaks. We were still able to see the metal atoms and cyanide ligands although the peaks in the Fourier map were quite diffuse. The mosaic character of the crystal would return to its original value when rehydrated. The change in lattice constant is in disagreement with that observed by Ludi,[5] but we feel the conditions employed by Ludi were not sufficient to completely dehydrate the crystals. The lattice constant change is also supported by Raman data[14] on hydrated and dehydrated crystals. When the crystals are dehydrated, a decrease in the N–Mn bond distance is observed, and a comparable decrease in the cyanide bond order is observed.[9] The structure of $Mn_3[Co(CN)_6]_2 \cdot CH_3OH$ has been undertaken and preliminary calculation indicates that the methyl alcohol molecules occupy sites similar to the water molecules.

Table II lists a compilation of bond distances for $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$. The Co–C distance of 1.882 (6) Å and C–N bond of 1.152 (11) Å are in complete agreement with corresponding distances in $Cs_2LiCo(CN)_6$.[9] The Mn–N distance of 2.184 (9) Å indicates a stronger interaction than that observed for Li–N.[9] The O–O bond distances possibly indicate the presence of four hydrogen bonds. There are two strong hydrogen bonds between O(1)–O(3) and O(3)–O(3) of 2.75 (5) and 2.62 (5) Å, respectively. The other two hydrogen bonds are much weaker and occur between O(1)–O(2) and O(2)–O(3) of 3.03 (6) and 2.91 (10) Å, respectively. A list of O–H distances and angles is given in Table III. All of the O–H distances fall around the expected value of 1.0(1) Å and all of the O···H bonds have an approximate value of 1.7 (1) Å. The H–O–H angles of 108° are quite close to the value expected for water molecules contained in a crystalline lattice (Ferraris and Franchini-Angela[15]). Brown[16] has recently shown that hydrogen bonds can be divided into two classes: (1) weak hydrogen bonds where the O—O distances are greater than 2.73 Å and the O—H···O angles tend to be close to 180°, (2) hydrogen bonds which have O—O distances less than 2.73 Å and angles significantly smaller than 180°. The bond distances and angles contained in Table III indicate that the two weak hydrogen bonds do indeed have O—O distances greater than 2.73 Å and O—H···O angles of 180°, and the two stronger hydrogen bonds have O—O distances equal to or less than 2.73 Å and O—H···O angles of 169 (1) and 125 (1)°.

Structure of $Cd_3[Co(CN)_6]_2 \cdot 12H_2O$

The structure of the Cd salt is identical with that of Mn as far as the metals, cyanides, and oxygen in 8c ($^1/_4$, $^1/_4$, $^1/_4$) are concerned. Some difference appears in the hydrogen bonding network. A list of positional and thermal parameters for the Cd structure is given in Table IV. It can be seen that the position of O(1) has refined from x = ca. 0.29 to 0.268 and O(3) has shifted to (0.217, 0.217, 0.217). The shift in the position of O(1) has also been observed in Raman studies by Swanson.[14] The Raman spectra for the Mn salt yielded very nearly octahedral symmetry around the Mn since the water molecule and nitrogen are almost exactly the same distance from the Mn. In the case of the Cd salt, distortion from octahedral symmetry was quite evident. This is borne out by a comparison of Cd–N and Cd–O distances of 2.27 (3)

Table IV. Positional and Thermal Parameters for $Cd_3[Co(CN)_6]_2 \cdot 12H_2O$

Atom	x	y	z	B, Å^2	β_{11}[a]	β_{22}	β_{33}	Occupancy
Cd	0	0	0.5	2.09 (5)				1
Co	0	0	0	1.68 (60)				$^2/_3$
C	0	0	0.1766 (14)		80	80	32	$^2/_3$
N	0	0	0.2860 (27)		153	153	39	$^2/_3$
O(1)	0	0	0.2618 (150)		588	588	150	$^1/_3$
O(2)	0	0	0	7.0				$^1/_3$
O(3)	0.217 (9)	0.217 (9)	0.217 (9)	7.0				$^1/_6$
O(4)	0.25	0.25	0.25	7.0				$^1/_3$

[a] All β's × 10^{-4}.

and 2.52 (16) Å, respectively. The shift of O(3) affects the hydrogen bonding scheme. The hydrogen bond distances now are O(1)–O(2) = 2.77 (16) Å, O(2)–O(3) = 3.99(30) Å, and O(1)–O(3) = 3.30 (25) Å. Although the standard deviations are high, it is clear the hydrogen bonding scheme must be different from that for the Mn salt. The other bond distances for Co–C and C–N of 1.872 (15) and 1.16 (3) Å are in good agreement with $Cs_2LiCo(CN)_6$. All of these bond distances are given in Table II.

There are several interesting points about this new model. The first is that the divalent metal now has octahedral, or close to octahedral, coordination in contrast to the model of Ludi.[4] Second, the hydrogen bonding structure seems to be quite important in stabilizing the structure. The implications of these results in regard to semipermeability are quite intriguing. From this model it appears that there are four possible factors involved in the transport mechanism. The four factors are σ-bonding properties, hydrogen-bonding capability, neutral charge, and size. It appears that any molecule which is charged or which is larger than 7.0 Å cannot enter the lattice. The other two factors appear to be of approximately the same importance. The mechanism of transport through the lattice appears to involve initially hydrogen bond formation between O_1 and O_3. The second step in the transport must involve the breaking of the original hydrogen bond and re-formation of the hydrogen bond with a different O_1. This might be accomplished through a temporary hydrogen bond with O_2. It appears from bonding energy considerations that O_1 is not transported through the lattice but is essential for transport of other water molecules.

Some calculations on the ordered model proposed by Weiser, Milligan, and Bates[3] have been carried out to determine how this completely ordered model refines in comparison to the disordered model proposed in this work. The two models were refined employing 160, 76, and 24 reflections. The 24 reflections were chosen because that is approximately the amount of data that was available from powder data. In a refinement of 24 reflections the ordered model gives a better *R* value and more reasonable C–N and Co–C bond distances. The only problem with the ordered model in this refinement was that the temperature factor on the interstitial divalent metal (8c, $^1/_4$, $^1/_4$, $^1/_4$) was quite high. This fact would not have been noticed in 1942, since temperature factors were not commonly refined at that time. The refinements of the data with all the reflections (160) point out the superiority of the disordered structure.

Table V compares observed and calculated crystal structure factors.

Acknowledgment. J.K. and I.B. acknowledge support from National Science Foundation Grant No. MPS-74-13718 and The Robert A. Welch Foundation Grant No. E-594. G.W.B. and W.O.M. also wish to acknowledge the Robert A. Welch Foundation Grant No. AA-668. We wish to thank Dr. F. A. Cotton for the use of the Syntex $P\bar{1}$ diffractometer. Also, we thank the Department of Chemistry at Brookhaven National Laboratory for the use of the neutron diffraction facilities and Dr. R. K. McMullan for help during data collection at BNL.

Registry No. $Mn_3[Co(CN)_6]_2 \cdot 12H_2O$, 63976-80-7; $Cd_3[Co(CN)_6]_2 \cdot 12H_2O$, 23540-99-0.

Supplementary Material Available: Listings of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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Complexes of the Platinum Metals. 10.[1] Dithioformato Derivatives of Ruthenium, Osmium, and Iridium

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Received January 24, 1977 AIC70063F

"Insertion" of carbon disulfide into platinum metal–hydrogen bonds has been employed to synthesize a range of new dithioformato complexes. Products prepared in this manner include the species $[MX(S_2CH)(CO)(PPh_3)_2]$ (two $[MX(RN\overset{\cdots}{-}CH\overset{\cdots}{-}S)(CO)(PPh_3)_2]$ M = Ru or Os; X = Cl, Br, or $OCOCF_3$), $[M(S_2CH)_2(PPh_3)_2]$, $[IrCl_2(S_2CH)(PPh_3)_2]$, $[MH(RN\overset{\cdots}{-}CH\overset{\cdots}{-}S)(CO)(PPh_3)_2]$, $[Ru(RN\overset{\cdots}{-}CH\overset{\cdots}{-}S)_2(PPh_3)_2]$, Phosphine substitution reactions have been employed to prepare the species $[MCl(S_2CH)(CO)(PMe_2Ph)_2]$ and $[MCl(S_2CH)(CO)(PMePh_2)_2]$. The stereochemistry of each new complex has been assigned by reference to the ^1H NMR spectrum of the dithioformate (S_2CH) ligands and has been confirmed where appropriate by use of high-field (metal hydride) resonances, virtual coupling patterns of the PMe_nPh_{3-n} ($n = 1$ or 2) ligands, or the ^{31}P NMR pattern of the phosphine ligands.

Introduction

Synthesis of the platinum carbon disulfide[2] and rhodium thiocarbonyl[3,4] complexes $[Pt(CS_2)(PPh_3)_2]$ and $[RhCl(CS)(PPh_3)_2]$, respectively, by Wilkinson et al. has stimulated much interest in the reactions of carbon disulfide with transition-metal species.[5] However, many of the products obtained are ill characterized, in particular their stereochemistry and structure are frequently not adequately established. We now find that the dithioformate anion, one of the ligands most commonly encountered in these systems,[5-8] can be detected and characterized by its IR and proton NMR spectra. Furthermore, couplings of the dithioformate central