Inorganica Chimica Acta, 21 (1977) 41–46

Complex Formation between Zinc, Cadmium and Mercury Dicyanides and 2,2′-Bipyridine, 1,10-Phenanthroline and 2,9-Dimethyl-1,10-phenanthroline. An Infrared Study

M. CANO, A. SANTOS and L. BALLESTER

Instituto de Química Inorgánica "Elhúyar", Facultad de Química, Universidad Complutense, Madrid-3, Spain

(Received May 11, 1976)

Zinc and cadmium cyanides form with 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (DMP) complexes of composition $M(CN)_2\cdot L$ *and* $M(CN)_2\cdot 2L$*, while* $Hg(CN)_2$ *forms only complexes of composition* $Hg(CN)_2\cdot L$ *with these molecules.*

The infrared spectra in the 4,000 to 20 cm^{-1} *region of all the complexes obtained have been studied. An attempt has been made to assign the* $\nu(M-C)$ *and* $\nu(M-N)$ *stretching frequencies in the low frequency region. Comparing a series of complexes having the same general formula and stereochemistry, correlations between the values of the* $\nu(M-C)$ *and* $\nu(M-N)$ *stretching frequencies and the acceptor and donor natures of the metal and ligand respectively could be established.*

The importance of steric factors has been demonstrated for complexes of composition $M(CN)_2\cdot 2L$*, being responsible for the inability of* $Zn(CN)_2$ *to coordinate with two molecules of DMP.*

Introduction

The formation of coordination complexes of Group II B metals by the reaction of donor ligands with metallic compounds R_2M (M = Zn, Cd, Hg; R = halogen, alkyl or aryl) is well known [1, 2]. The acceptor capacity of the metal increases with the electronegativity of R [3, 4] as increasing this increases the polarity of the M–R bond. Thus the ability to perform donor–acceptor reactions, which give rise to the formation of complexes of generally higher coordination number, varies in the order halogen > aryl > alkyl. It is to be expected that the CN^- anion linked to the metal will give rise to strong interactions due to the relatively high polar character of the M–C bond.

In the present paper the donor–acceptor interaction has been studied in a series of complexes of composition $M(CN)_2\cdot L$ and $M(CN)_2\cdot 2L$ (L = bipy, phen and DMP) using infrared spectroscopy principally to determine the $\nu(M-C)$, $\nu(C\equiv N)$ and $\nu(M-N)$ stretching frequencies. To obtain these it was thus necessary to interpret the complete infrared spectra. By comparing the values of these frequencies in complexes with the same general formula and stereochemistry it is possible to determine the correlation between these values and the acceptor and donor capacities of the metal and ligand respectively.

Of all the complexes here studied, only the two complexes of mercury of formula $Hg(CN)_2\cdot L$ (L = bipy, phen) have been described in the literature, and their infrared spectra in the 4,000 to 200 cm^{-1} region have been reported [5].

Experimental

Materials

Mercury cyanide (Scharlau), 2,2′-bipyridine (Merck), 1,10-phenathroline (Merck) and 2,9-dimethyl-1,10-phenanthroline (Merck) are available commercially and were used without prior purification. The cyanides of Zn and Cd were prepared as described in the literature [6].

Preparations

Complexes of Zn, Cd and Hg Cyanides with 2,2′-Bipyridine

The complexes of formula $Zn(CN)_2\cdot 2$bipy, $Cd(CN)_2\cdot$bipy and $Hg(CN)_2$bipy were obtained by adding slowly, with stirring, a solution of bipyridine in methanol to a solution of $Zn(CN)_2$ or $Cd(CN)_2$, both in aqueous NH_3, or to a solution of $Hg(CN)_2$ in methanol. The molar ratio of reagents was 1:1 in every case.

$Zn(CN)_2\cdot 2$bipy was isolated in the form of yellow crystals by crystallisation from the solution formed by mixing the two starting reagents. These crystals were purified by washing with water and a few drops of aqueous NH_3. On dissolving this product in methanol or ethanol, a white crystalline powder precipitated after a short time which after isolation, washing with ether and drying in a high vacuum corresponded to the formula $Zn(CN)_2\cdot$bipy.

The compounds $Cd(CN)_2\cdot$bipy and $Hg(CN)_2\cdot$bipy are white microcrystalline products that precipitate immediately on mixing the reactants.

TABLE I. Analytical Results.

Compounds	Melting Point °C[a]	M%		C%		H%	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
$Zn(CN)_2$·bipy (polymer)	208–10	23.89	23.70	52.64	52.70	2.92	2.82
$Zn(CN)_2$·bipy	135	15.21	15.43	61.43	60.71	3.72	3.89
$Zn(CN)_2$·phen	300 D	21.96	21.82	56.46	55.72	2.68	2.44
$Zn(CN)_2$·2 phen·$5H_2O$	194 D	11.51	11.73	54.94	54.97	4.58	5.01
$Zn(CN)_2$·DMP	330 D	20.08	20.30	68.91	68.58	3.60	4.00
$Zn(CN)_2$·2 DMP·H_2O	280 D	11.85	12.00	65.29	64.94	4.71	4.80
$Cd(CN)_2$·bipy	274–9	35.05	35.18	44.91	45.10	2.49	2.60
$Cd(CN)_2$·2 bipy	269	23.57	23.36	55.37	55.35	3.35	3.36
$Cd(CN)_2$·2 phen	312 D	21.41	21.30	59.44	59.51	3.04	2.97
$Cd(CN)_2$·DMP	300 D	30.16	30.10	51.55	51.53	3.22	3.45
$Cd(CN)_2$·2 DMP		19.36	19.17	62.02	61.77	4.13	4.20
$Hg(CN)_2$·bipy	240	49.06	48.97	35.24	35.31	1.25	1.28
$Hg(CN)_2$·phen	355 D	46.34	46.21	38.36	38.44	1.96	1.98
$Hg(CN)_2$·DMP	270 D	43.50	43.57	41.68	41.75	2.68	2.92

[a] D, decomposed.

If the same reaction described above is carried out in 1:2 molar proportion of metal cyanide to ligand, the compounds $M(CN)_2$·2bipy (M = Zn, Cd) are formed which can be isolated by crystallisation. In the case of $Hg(CN)_2$, $Hg(CN)_2$·bipy is obtained.

The chemical analysis of these complexes and other properties are given in Table I.

Complexes of Zn, Cd and Hg Cyanides with 1,10-Phenanthroline and 2,9-Dimethyl-1,10-phenanthroline

The procedure to obtain the complexes of composition $M(CN)_2$·L and $M(CN)_2$·2L with these ligands is analogous to that described for the bipyridine compounds except that the solvent used for the ligands was in this case ethanol. The results of the analysis of the products obtained and other properties are also given in Table I.

It was not possible to isolate $Cd(CN)_2$·phen nor $Cd(CN)_2$·2DMP, although the latter seemed to form on washing the corresponding complex of 1:1 composition with a concentrated aqueous NH_3 solution. In the case of $Hg(CN)_2$ only complexes of composition $Hg(CN)_2$·L have been isolated. All the complexes obtained were white crystalline solids.

Analytical Methods

Carbon and hydrogen were determined by organic microanalysis with a Coleman Model 33, carbon–hydrogen analyzer. Zinc and cadmium were determined by complexometric titrations with EDTA, using Merck buffer tablets as indicator. Mercury was determined gravimetrically as sulphide.

Physical Measurements

I.r. spectra in the 4,000–200 cm^{-1} region were recorded on a Perkin–Elmer 325 spectrophotometer from Nujol mulls supported between CsI plates and KBr pellets. Far infrared spectra in the 400–20 cm^{-1} region were recorded on a Beckman Fourier spectrophotometer model IR-720 from polyethylene pellets.

Raman spectra in the solid phase were recorded using a Jarrell Ash. Model 165 spectrometer and the 4,480 Å line of an Ar^+ laser at 100 mW.

Differential Thermal Analysis (DTA) was carried out with a Dupont Thermoanalyzer, model 990.

Results and Discussion

Analytical Data

The analytical data of the different products obtained showed that the direct reaction of Zn, Cd and Hg cyanides with bipy, phen and DMP in 1:1 molar proportions gives rise to the following complexes:

$Zn(CN)_2$·2bipy $Zn(CN)_2$·phen $Zn(CN)_2$·DMP
$Cd(CN)_2$·bipy $Cd(CN)_2$·2phen $Cd(CN)_2$·DMP
$Hg(CN)_2$·bipy $Hg(CN)_2$·phen $Hg(CN)_2$·DMP

If the reaction is performed with a 1:2 molar proportion of reagents, complexes of the following compositions are formed:

$Zn(CN)_2$·2bipy $Zn(CN)_2$·2phen
$Zn(CN)_2$·2DMP·H_2O
$Cd(CN)_2$·2bipy $Cd(CN)_2$·2phen $Cd(CN)_2$·DMP
$Hg(CN)_2$·bipy $Hg(CN)_2$·phen $Hg(CN)_2$·DMP

Since $Zn(CN)_2$·bipy is obtained on dissolving methanol or ethanol the corresponding complex of

1:2 composition, the solubilities in the reaction medium of the different complexes that form are thought to be very important. Similarly $Cd(CN)_2 \cdot 2DMP$ does not form in the direct reaction, but on washing $Cd(CN)_2 \cdot DMP$ with aqueous NH_3. The fact that $Cd(CN)_2 \cdot$phen has not been isolated may be attributed also to the lower solubility of $Cd(CN)_2 \cdot 2$phen in the reaction medium used and in other common solvents.

However, it is not surprising that only Hg complexes of composition $Hg(CN)_2 \cdot L$ have been obtained as Hg normally exhibits a lower tendency to six-coordination than Cd or Zn.

Infrared Spectra

Infrared spectral data in the 4,000–20 cm^{-1} region for the various complexes were recorded. Table II gives the most significant infrared frequencies of these complexes in the 4,000–440 cm^{-1} region and the frequencies of all the bands which appear below 440 cm^{-1}.

In the i.r. spectra of the various complexes shifts of the characteristic ligand bands towards higher frequencies in the 1,400–1,600 cm^{-1} region and splitting of the strong bands that appear between 700 and 850 cm^{-1} for bipy, phen and DMP were observed. These effects are similar to those described by Schilt and Taylor [7] and attributed to ligand coordination. These i.r. ligand frequencies are not included in Table II.

The bands corresponding to the $\nu(C{\equiv}N)$ stretching frequency in the 2,100 to 2,200 cm^{-1} region appear displaced to lower frequencies with respect to those of the starting metal cyanide and are, in the majority of cases, of small intensity. In the i.r. and Raman spectra of $Zn(CN)_2 \cdot$phen and $Zn(CN)_2 \cdot DMP$ bands are not observed in this region. The frequencies of the only three bands that are found in the i.r. spectra of zinc and cadmium cyanides are, respectively, 2217, 450, 194 cm^{-1} and 2196, 2170, 400, 125 cm^{-1}. The high value of the $\nu(C{\equiv}N)$ stretching frequency in $Zn(CN)_2$ and in $Cd(CN)_2$ is caused by the polymeric structure with cyanide bridging groups of these compounds [8].

The bands corresponding to the M–C stretching vibrations have been assigned taking into account the frequencies at which these bands appear in the starting cyanides and in the corresponding tetracyano complexes [9]. It is assumed that for tetracoordinate species these vibrations must lie at frequency values in between these two. For the hexacoordinate species the $\nu(M–C)$ stretching frequencies must appear at lower values than in the corresponding tetracoordinate species.

In the lower than 400 cm^{-1} frequency region the bands corresponding to the deformation vibrations of the $M–C{\equiv}N$ bonds and the stretching and bending vibrations of the M–N bonds must appear. The assignment of this spectral region requires special care, owing to the scant literature information available concerning the $\nu(M–N)$ vibrations. It must also be taken into account that ligands vibrations activated by coordination give rise to bands in this region, as shown by Hutchinson *et al.* [10] which can lead to incorrect assignment of the $\nu(M–N)$ stretching frequencies. These bands are those designated by the symbols L(B), L(C) and L(D). The L(A) and L(F) bands are free ligand bands that fall in the same range and are slightly displaced by coordination. The assignment of the $\nu(M–N)$ stretching vibration has accordingly been attempted by comparison with the assignments achieved for the $[ML_3]^{2+}$ [10] and MLX_2 [11] complexes (X = halogen, L = bipy, phen) of the same metals using metal isotopic displacement methods.

In the assignment of the bands corresponding to the $\delta(MCN)$ bending vibrations, it has been assumed that in the $M(CN)_2 \cdot L$ tetracoordinate species these vibrations must appear at higher frequencies than the corresponding vibrations in the $[M(CN)_4]^{2-}$ species [9] and that in the $M(CN)_2 \cdot 2L$ complexes these vibrations must appear at lower frequencies than those assigned to the respective $M(CN)_2 \cdot L$ species.

Several of the complexes obtained were isolated as hydrated species. In the case of the $Zn(CN)_2 \cdot 2bipy \cdot H_2O$, $Zn(CN)_2 \cdot 2phen \cdot 5H_2O$ and $Cd(CN)_2 \cdot DMP \cdot H_2O$ the water was present as water of crystallisation and could be eliminated at low temperatures to yield the dehydrated form whose i.r. spectra differed from that of the hydrated form only as would be expected on the disappearance of the bands due to water. However, in the $Zn(CN)_2 \cdot 2DMP \cdot H_2O$ complex the water seemed to have a special position. The DTA curve showed endothermic peaks at 107 and 137 °C. The i.r. spectrum of the sample heated to the temperature of the first endothermic peak corresponded to a mixture of $DMP \cdot 1/2H_2O$ and the complex $Zn(CN)_2 \cdot DMP$. On the other hand, there was hardly any difference between the frequencies corresponding to the Zn–C stretching vibrations in both complexes. This seems to indicate that the second molecule of DMP is not directly bonded to the metal, but across water molecules. It was also noticeable that in this complex there is a particularly intense libration of water of crystallisation at 550 cm^{-1}.

Probable Structures of the Complexes

Although it is not possible to obtain complete structural information from infrared spectra of complexes, it is possible to deduce some structural features.

Up to date structural data of only the $Zn(CN)_2 \cdot DMP$ [12] and $Hg(CN)_2 \cdot$bipy [13] complexes have been determined and both of these are tetracoordinate species in which the metal atom occupies

TABLE II. Infrared Spectral Results (cm^{-1} in Nujol mulls and polyethylene discs) and Tentative Band Assignments: $M(CN)_2 \cdot L$ and $M(CN)_2 \cdot 2L$ Complexes (M = Zn, Cd, Hg; L = bipy, phen, DMP; bands of ligands in the 4,000–440 cm^{-1} region are not included).[a]

Bipy	$Zn(CN)_2 \cdot$bipy	$Zn(CN)_2 \cdot 2$bipy$\cdot H_2O$	$Cd(CN)_2 \cdot$bipy	$Cd(CN)_2 \cdot 2$bipy	$Hg(CN)_2 \cdot$bipy	phen$\cdot H_2O$	$Zn(CN)_2 \cdot$phen
		3,450m ν(OH)				3,515m ν(OH)	
		3,400m ν(OH)				3,265m ν(OH)	
	2,172s ν(CN)	2,142w ν(CN)	2,160w ν(CN)	2,120vw ν(CN)	2,160m ν(CN)		–
	2,158sh ν(CN)	2,133sh ν(CN)	2,142w ν(CN)				
		1,635m δ(HOH)				1,640m,b δ(HOH)	
404s L(A)	412m L(A)	415m L(A)	413s, 407m L(A)	414w, 405s L(A)	412sh L(A)	412m L(A)	428m L(A)
	384s, 378sh ν(MC)				395vs, 385sh ν(MC)		402s ν(MC)
		354s ν(MC)					359m ν(MC)
	346m L(B)	346m L(B)	340vs ν(MC)+L(B)	349w L(B)			
		340m,b ν(MC)	324sh ν(MC)				
	326m δ(MCN)						
	315sh δ(MCN)	312s δ(MCN)			318w δ(MCN)		310s δ(MCN)
		300sh δ(MCN)					
	280sh L(C)	288sh L(C)					290s L(B)
	267m δ(MCN)		262s δ(MCN)	274s,b ν(MC)	273m δ(MCN)		274s δ(MCN)
	252w L(D)		250w L(D)	256w L(D)			270sh δ(MCN)
	246w L(D)		243m δ(MCN)+L(D)	240vs δ(MCN)+L(D)		240s L(C)	241s L(C)
	230s L(D)	235s,b L(D)	233m L(D)				
	218sh ν(MN)		208s δ(MCN)	210s δ(MCN)		208w L(D)	205sh L(D)
	195sh L(E)	196sh ν(MN)	198s L(E)	198m L(E)		196w*L(D)	198m ν(MN)+L(D)
	182vs ν(MN)+L(E)	180vs ν(MN)+L(E)				184w*L(D)	178sh ν(MN)+L(D)
		168sh L(F)	174sh L(F)	170sh L(F)		174w*L(D)	174s L(D)
164s L(F)	168s L(F)	152m ν(MN)	164s ν(MN)				
136m*	142w L	138m L	138s ν(MN)	142s,b ν(MN)+L	138s,b ν(MN)+L	122s*	128sh L
			130sh L				
116m	124w L	124m L	124sh, 116s L	120s ν(MN)			116sh L
96s*	107w L		104m L	114s,b L + ν(MN)?	87s L	110s*	110s L

$Zn(CN)_2 \cdot 2phen \cdot 5H_2O$	$Cd(CN)_2 \cdot 2phen$	$Hg(CN)_2 \cdot phen$	DMP.1/2H_2O	$Zn(CN)_2 \cdot DMP$	$Zn(CN)_2 \cdot 2DMP \cdot 5H_2O$	$Cd(CN)_2 \cdot DMP$	$Cd(CN)_2 \cdot 2DMP$	$Hg(CN)_2 \cdot DMP$
3,365m,b ν(OH)			3,362m,b ν(OH)		3591m, 3501m ν(OH)			
					3401m, 3221m ν(OH)			
2,137w ν(CN)	2,126vw ν(CN)	2,165w ν(CN)		–	2,146w ν(CN)	2,160w ν(CN)	2,127w ν(CN)	2,163vw ν(CN)
1,650m,b δ(HOH)					1,641m,b δ(HOH)			
			572w H_2O lib.		571m,b H_2O lib.			
			512w,b H_2O lib.		511w,b H_2O lib.			
421m L(A)	416s L(A)	418s L(A)	424m L(A)	435m L(A)	436m L(A)	433 m L(A)	435m L(A)	428m L(A)
				418m L(A)	426w L(A)	399m L(A)	395w L(A)	
		400vs ν(MC)		399s ν(MC)	388s ν(MC)			412vs ν(MC)
		380sh ν(MC)		360s ν(MC)	364s ν(MC)			393m ν(MC)
353s ν(MC)					330m δ(MCN)	344s ν(MC)		324m δ(MCN)
312s δ(MCN)		312w δ(MCN)		311s δ(MCN)	314s δ(MCN)	324s ν(MC)	314w L(B)	311w δ(MCN)
307sh δ(MCN)								
288s L(B)	297sh L(B)		298s L(B)	290s L(B)	300s L(B)	292sh L(B)	287s ν(MC)+L(B)	
	290s ν(MC)				287s L(B)	284sh L(B)		
274sh δ(MCN)	274m δ(MCN)	272w δ(MCN)		268s δ(MCN)+L(C)	268s δ(MCN)+L(C)			276m δ(MCN)
262w L(C)	260m L(C)					259m δ(MCN)	260vw L(C)	
244sh L(C)	246s L(C)		250m* L(C)		246w L(C)	250m δ(MCN)	252w δ(MCN)	
						243sh L(C)	248w δ(MCN)	
240m L(C)	236m δ(MCN)	238s L(C)	234s L(C)			224m L(C)	243m L(C)	
205sh L(D)	200w L(D)			208 m ν(MN)	210w ν(MN)	211m δ(MCN)		
191vs ν(MN)+L(D)	194w L(D)			194sh L(D)	180s ν(MN)	182w L(D)		
172s ν(MN)+L(D)	160s L(D)	156s L(D)	172sh L(D)	174s ν(MN)+L(D)	174sh L(D)	167s ν(MN)+L(D)		174s L(D)
148m ν(MN)	152s ν(MN)	144s ν(MN)	160s* L(D)	164sh L(D)	153m L(D)	146m ν(MN)		140s,b ν(MN)
	140s ν(MN)	136s ν(MN)						
114sh L	114vs L+ν(MN)?		124vs*	114s L	110s L	116m L		110w L
108s L	104s L	86s L	107m	100s L	102s L	102m L		104w L
								83s L

---

[a] s, strong; m, medium; w, weak; sh, shoulder; v, very; b, broad; L, ligand; *, disappears or diminishes in solution; lib, libration.

the centre of a distorted tetrahedron and the cyanide groups are terminal. In the first of these compounds the Zn–N and Zn–C bond lengths are 2.070 Å and 1.990 Å respectively, while the N–Zn–N and C–Zn–C angles are 81.3° and 121.7° respectively. The little precision with which the interatomic distances in $\mathrm{Zn(CN)_2}$ have been determined does not permit a critical comparison between the Zn–C and Zn–N bond lengths in both compounds. The similarity of the i.r. spectra of the $\mathrm{M(CN)_2{\cdot}L}$ compounds of the same metal also seems to suggest that the stereochemistry is similar in all these compounds, the central atom having C_{2v} microsymmetry.

An analysis of the number of C≡N and M–C stretching bands that appear in the i.r. spectra gives additional structural information on the *cis-* or *trans*-configuration of the hexacoordinate complexes of composition $\mathrm{M(CN)_2{\cdot}2L}$. One band for the ν(C≡N) and ν(M–C) stretching frequencies will be found if the complex is *trans* (D_{2h}) while there will be two if the complex is *cis* (C_2). This test is conclusive only if one band is found, since the other stretching vibration could be activated by site symmetry effects in the solid. Accordingly all the complexes of composition $\mathrm{M(CN)_2{\cdot}2L}$ are thus probably in the *trans* configuration, except for $\mathrm{Zn(CN)_2{\cdot}}$2bipy which could be *cis*.

It is significant that the complex of composition $\mathrm{Zn(CN)_2{\cdot}2DMP}$ in which the two ligand molecules are coordinated to the metal is not obtained, but instead a hydrate in which the second ligand molecule seems to be bound across the water molecule. This result seems to have its origin in a steric hindrance effect which is greater than in the $\mathrm{Cd(CN)_2{\cdot}2DMP}$ case.

Donor–Acceptor Interaction

The reaction between the $\mathrm{M(CN)_2}$ compounds, considered as acceptors, and the donor ligands bipy, phen and DMP gives rise to new species in which, for complexes of the same metal, the coordination number is the principal factor responsible for the shifts in the ν(M–C) and ν(C≡N) stretching frequencies.

In complexes of the same composition it is observed that the ν(M–C) and ν(C≡N) stretching frequencies have higher values in the Zn and Hg complexes than in the Cd ones. This variation is similar to that observed in the corresponding tetracyano complexes of these metals and can be attributed to the variation in the ionic–covalent character of the metal–carbon bond.

In the absence of other effects, the donor–acceptor interaction also affects the values of these ν(M–C) and ν(C≡N) frequencies, as can be seen by comparing these values in a series of complexes of the same metal, composition and stereochemistry. Thus in the $\mathrm{M(CN)_2{\cdot}L}$ and $\mathrm{M(CN)_2{\cdot}2L}$ complexes the donor–acceptor interaction, evaluated on the basis of the lowering of the ν(M–C) stretching frequency, varies generally in the order DMP > phen > bipy. The anomalous lowering of ν(M–C) for $\mathrm{Zn(CN)_2{\cdot}}$bipy and $\mathrm{Cd(CN)_2{\cdot}}$2bipy seems to indicate a more effective coordination of the ligand bipy with the metal. This result can be explained on taking into account that free rotation is possible around the axis that joins the two bipyridine rings. This rotation cannot occur for the other two rigid ligands.

It can be thought that the ν(M–N) stretching frequencies may be a more direct indication of the donor–acceptor interaction. The problem is to obtain a correct assignment for these frequencies, and the criteria mentioned earlier have been followed to achieve this purpose. On comparing the ν(M–N) stretching frequencies it is deduced that in the complexes with the same composition and the same ligand, the strongest donor–acceptor interactions are observed in the Zn complexes. This is in agreement with a hard–hard interaction in the Zn case, which will be stronger than the hard–soft interaction in the Hg complexes.

In the tetracoordinate complexes of the same metal, the effect of the different ligand is very similar, however, slight differences appear that agree in general with the variation in donor character of the ligands.

Acknowledgments

Thanks are given to Prof. García Blanco, Orza Segade and coworkers of the Rocasolano Institute for the crystalline structure determination of two of these compounds and for the use of the Raman spectrometer respectively. We are grateful to Dr. Rojas López for critical discussions on various aspects of this work. We are also indebted to Dr. B. G. Mellor for help with the translation into English.

References

1 K. H. Thiele and P. Zdunneck, *Organomet. Chem. Rev., 1,* 331 (1966).

2 A. J. Canty and G. B. Deacon, *J. Organomet. Chem., 49,* 125 (1973).

3 W. Strohmeier and K. Nützel, *Z. Elektrochem., 62,* 188 (1958).

4 V. G. Noltes and J. W. G. Van der Hurk, *J. Organomet. Chem., 3,* 222 (1965).

5 S. C. Jain and R. Rivest, *Inorg. Chim. Acta,* 4, 291 (1970).

6 G. Brauer, 'Química Inorgánica Preparativa', Reverté, Barcelona, 1958.

7 A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem., 9,* 211 (1959).

8 H. S. Zhanov, *C.R. Acad. Sci. USSR, 31,* 352 (1941).

9 L. H. Jones, 'Inorganic Vibrational Spectroscopy', Vol. I, Dekker, New York, 1971.

10 B. Hutchinson, J. Takemoto and K. Nakamoto, *J. Am. Chem. Soc., 92,* 3335 (1970).

11 R. E. Wilde and T. K. K. Srinivasan, *J. Inorg. Nucl. Chem., 36,* 323 (1973).

12 M. Martínez Ripoll, S. García Blanco and M. A. Monge, private communication.

13 J. Fayos and S. García Blanco, private communication.