Eight-co-ordination. Part V.[1] Tetracyanotetrakis(alkyl isocyano)-molybdenum(IV) and -tungsten(IV): Pseudo-Cubic Complexes

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The diamagnetic, nonelectrolytic complexes $M(CN)_4(CNR)_4$ (M = Mo or W; R = Me, Et, Pr^n, Pr^i, Bu^t, or CPh_3) give unexpectedly simple i.r. and Raman spectra in the C–N stretching region. On the basis of *X*-ray data for $Mo(CN)_4(CNMe)_4$, all the complexes are presumed to have dodecahedral configurations.

CONSIDERABLE interest attaches to the stereochemistry of eight-co-ordination.[2] For complexes of the *d*-block metals, two basic co-ordination polyhedra are observed, *viz.* the triangular dodecahedron and the square Archimedean antiprism. The configuration of highest symmetry, the cube, has never been observed for discrete complexes, and has been shown to be unstable with respect to the two other configurations.[3,4] The two preferred configurations differ little in energy and it appears that small changes in the environment of the complex may be sufficient to alter the favoured form. For instance, it has been suggested that the $M(CN)_8^{4-}$ ions (M = Mo or W), which are well known to adopt the dodecahedral configuration in solid salts,[5] may be antiprismatic in aqueous solution,[1,6] although this view has been challenged recently.[7] Similarly, the $W(CN)_8^{3-}$ ion has the dodecahedral configuration in the tetrabutylammonium salt [8] but in the hydrated sodium salt the alternative form is adopted [9] and appears also in the $Co(NH_3)_6^{3+}$ salt [1] and in aqueous solution.[10]

Of particular interest are derivatives of the type MA_4B_4, of which all known examples have the dodecahedral configuration.[2] This stereochemistry provides two naturally-differentiated sites for the two types of ligand. Derivatives originally thought to be of the type $M(CN)_4(OH)_4^{4-}$ (M = Mo or W) have been shown to contain six-co-ordinate metals,[11] but the complexes $M(CN)_4(CNR)_4$, first prepared by Hölzl,[12] have recently been characterised as genuinely eight-co-ordinate.[13] The stereochemistry of these complexes is not known. We have investigated complexes with a variety of R-groups in the hope that the use of very large groups might force an approximately cubic configuration.

EXPERIMENTAL

The complexes were prepared by prolonged refluxing (8—48 h) of the salts $Ag_4M(CN)_8$ (freshly prepared) with the appropriate organic halide (see Table 1). For the trityl derivatives a solution of trityl chloride in chloroform or benzene was used. The residual solid was removed by filtration and extracted with chloroform or the organic halide. The extract and filtrate were combined and concentrated, and the complexes were precipitated by the addition of ether. Maximum yields were obtained by finely grinding the silver salt. Reaction appears to be terminated by the formation of an impervious coating of silver halide on the octacyanide. Most of the complexes are readily soluble in the common polar organic solvents, from which they can be precipitated by addition of ether. The methyl derivatives are only sparingly soluble, and were extracted with, and recrystallised from hot water. Representative complexes were found to be monomeric (benzene or ethanol solutions), diamagnetic (Gouy, n.m.r., or e.s.r.) and non-conducting ($\Lambda_M < 5\Omega^{-1}$ cm^2 l^{-1} in nitrobenzene). In some cases, weak e.s.r. signals were obtained from the solid complexes, but these were eliminated by careful recrystallisation. Some degradation occurs on standing, particularly on exposure to light.

Attempts were made to prepare complexes of stoicheiometry other than $M(CN)_4(CNR)_4$ from reactions between $K_4M(CN)_8$ and dimethyl sulphate, or by refluxing $Hg_2W(CN)_8$ or a mixture of $W(CN)_4(CNEt)_4$ and HgI_2 with an excess of ethyl iodide. In no case was it possible to isolate novel materials. Refluxing the complexes with an excess of triphenylphosphine oxide or pyridine gave tarry mixtures from which no useful products could be obtained. The complexes decomposed on treatment with oxidising agents [$Ce(SO_4)_2$ or $KMnO_4$].

I.r. spectra were obtained using Perkin-Elmer 125 and 257 spectrometers. Raman spectra of the solids were measured with the Cary 81 laser spectrometer at the University of Southampton; the complexes were not sufficiently soluble for spectra of solutions to be obtained.

RESULTS AND DISCUSSION

The reaction between the salts $Ag_4M(CN)_8$ (M = Mo or W) and alkyl halides leads to the molecular complexes $M(CN)_4(CNR)_4$ (R = Me, Et, Pr^n, Pr^i, Bu^t, or CPh_3), as suggested previously.[12,13] The methyl compounds were

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[1] R. V. Parish, P. G. Simms, M. A. Wells, and L. A. Woodward, *J. Chem. Soc.* (*A*), 1968, 2882.

[2] R. V. Parish, *Co-ordination Chem. Rev.*, 1966, **1**, 439; S. J. Lippard, *Progr. Inorg. Chem.*, 1967, **8**, 109; E. L. Muetterties and C. M. Wright, *Quart. Rev.*, 1967, **21**, 109.

[3] D. L. Kepert, *J. Chem. Soc.*, 1965, 4736; R. V. Parish and P. G. Perkins, *J. Chem. Soc.* (*A*), 1967, 345.

[4] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235.

[5] J. L. Hoard, T. A. Hamor, and M. O. Glick, *J. Amer. Chem. Soc.*, 1968, **90**, 3177.

[6] H. Stammreich and O. Sala, *Z. Elektrochem.*, 1960, **64**, 741; *ibid.*, 1961, **65**, 149; K. O. Hartman and F. A. Miller, *Spectrochim. Acta*, 1968, **24***A*, 669; E. König, *Z. Naturforsch.*, 1968, **23***A*, 853.

[7] T. V. Long and G. A. Vernon, *J. Amer. Chem. Soc.* 1971, **93**, 1919.

[8] B. J. Corden, J. A. Cunningham, and R. Eisenberg, *Inorg. Chem.*, 1970, **9**, 356.

[9] L. D. C. Bok, J. G. Leipoldt, and S. S. Passon, *Acta Cryst.*, 1970, **B26**, 684.

[10] B. R. McGarvey, *Inorg. Chem.*, 1966, **5**, 476; R. G. Hayes, *J. Chem. Phys.*, 1966, **44**, 2210.

[11] S. J. Lippard, H. Nozaki, and B. J. Russ, *Chem. Comm.*, 1967, 118; V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, 1968, **90**, 3374; R. V. Parish and P. G. Simms, unpublished observations.

[12] F. Hölzl and G. I. Xenakis, *Monatsh.*, 1927, **48**, 689; F. Hölzl and N. Zymaris, *ibid.*, 1928, **49**, 241.

[13] H. Latka, *Z. anorg. Chem.*, 1967, **353**, 243.

TABLE 1

Characteristics and reagents for the complexes $M(CN)_4(CNR)_4$. Calculated analytical figures in parentheses

M	R	Dec. Pt. (°C)	Reagent	C (%)	H (%)	N (%)	*M*
Mo	Me	190—197	MeI	39·2 (39·5)	3·3 (3·3)	30·6 (30·7)	
	Et	120—125	EtI	45·6 (45·3)	4·7 (4·8)	27·1 (26·6)	
	Pr^n	140—146	Pr^nBr	50·0 (50·4)	6·1 (5·9)	23·0 (23·5)	
	Pr^i	135—140	Pr^iBr	50·7 (50·4)	5·7 (5·9)	22·8 (23·5)	
	Bu^t	172—177	Bu^tCl	54·5 (54·1)	6·8 (6·8)	20·3 (21·0)	516 [a] (532)
	Ph_3C	180—185	Ph_3CCl	77·0 (79·0)	4·8 (4·7)	8·5 (8·8)	
W	Me	216—220	MeI	31·6 (31·8)	2·7 (2·7)	24·7 (24·8)	
	Et	140—145	EtI	37·8 (37·8)	4·0 (4·0)	22·0 (22·0)	495 [a] 506 [b] (508)
	Pr^n	160—165	Pr^nBr	42·5 (42·6)	5·1 (5·0)	19·7 (19·9)	628 [b] (564)
	Pr^i	155—159	Pr^iBr	42·4 (42·6)	5·0 (5·0)	19·8 (19·9)	
	Bu^t	195—200	Bu^tCl	46·3 (46·4)	5·7 (5·8)	17·0 (18·1)	698 [b] (620)
	Ph_3C	200—205	Ph_3CCl	74·0 (73·9)	4·6 (4·4)	8·0 (8·2)	1340 [a] (1364)

[a] In benzene. [b] In ethanol.

TABLE 2

C–N Stretching frequencies (cm^{-1}) for $M(CN)_4(CNR)_4$. Isotope bands are italicised. Figures in parentheses are full widths at half-height

	M = Mo			M = W		
	Infrared		Raman	Infrared		Raman
R	$CHCl_3$	Solid [a]	Solid	$CHCl_3$	Solid [a]	Solid
Me		*2096*w,b			*2099*vw,b	
					*2115*vvw,b	
	2144w(16)	2142m(4)	2146s(6)		2145m(5)	2149m(8)
		*2194*vw,b			*2188*vvw,sh	
		2208vvw,sh			*2202*vvw,sh	
		2232vs			2232vs	
	2246vs(16)	} (42)	2241vs(12)		} (52)	2234vs(8)
		2247vs			2245vs	
			2263vs(10)		2260vvw,sh	2260s(7)
Et	2138m(10)	2137m(6)	2142s(7)	2144m(12)	2139m(8)	2144s(10)
		*2142*vvw,sh			*2144*vvw,sh	
	*2190*w,b	*2185*vw,b		*2195*w,b	*2190*w,b	
		2220vs			2216vs	
	2224vs(16)	} (37)	2228s(8)	2225vs(16)	} (38)	2223vs(12)
		2230vs			2227vs	
		2250vvw,sh	2248vs(10)		2247vvw,b	2248s(10)
Pr^n			2144s	2145w(11)	2143m(4)	2147s(7)
					*2182*vw,b	
			2228s	2221vs(16)	2220vs(25)	2223vs(11)
			2244s			2246m(11)
Pr^i	2136m(10)	2143m(7)	2144s(6)	2145m(10)	2143m(7)	2147m(10)
		*2149*vw,sh			2151w,sh	
	*2174*vvw,b	*2185*vw,b		*2178*vw,b	*2170*vw,b	
	2210vs(22)	2214vs(60)	2218vs(8)	2209vs(16)	2205vs(29)	2210vs(20)
	2233vvw,b		2239m(4)	2237vw,b	2234vw,b	2238s(16)
Bu^t	2136m(8)	2136m(6)	2143vs(6)	2144m(9)	2141mw(6)	2145m(8)
	*2166*vvw,b	*2170*vvw,b			*2145*vvw,sh	
	2203vs(28)	2204vs(58)	2210s(16)	2203vs(25)	2203vs(41)	2208vs(22)
		2236vvw,b	2234vs(8)		2223vvw,b	2232s(12)
CPh_3		2133w(4)			2136w(4)	2138w(3)
					2138vvw,sh	
		2140w(3)		2145w(14)	2143w(3)	2146w(3)
					2146vvw,sh	
		*2174*vw,b			*2172*vvw,b	
		2211vs(24)		2211vs(29)	2205vs(47)	2207vs(9)
		2236vvw,b			2238vvw,b	2235vs(6)

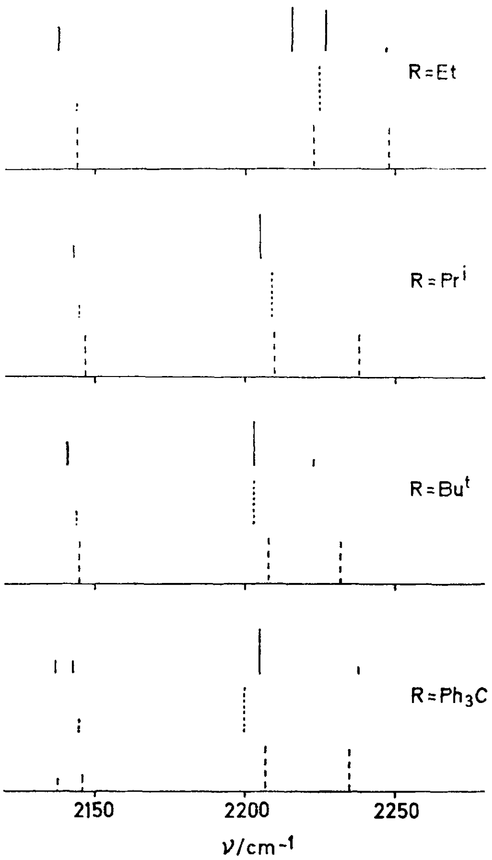
[a] Nujol or hexachlorobutadiene mulls.

reported to be hydrates, but our derivatives all appear to be anhydrous. No evidence of intermediates containing less isonitrile groups or of further reaction to introduce more such groups was found under a variety of conditions, although the seven-co-ordinate molybdenum(II) complexes $MoX_2(CNR)_5$ (X = Cl or Br; R = cyclohexyl, *p*-tolyl) and $[MoI(CNMe)_6]I$ have recently been reported.[14] The molybdenum(IV) and tungsten(IV) complexes thus differ from other metal cyanide-isonitrile systems, *e.g.* those of iron, in which derivatives of various stoicheiometries may be obtained.[15] In contrast to the parent complexes, $M(CN)_8^{4-}$, it is also not possible to obtain one-electron oxidation products; all attempts at oxidation led to decomposition.

In an attempt to elucidate the stereochemistry of the complexes $M(CN)_4(CNR)_4$, we have examined the i.r. and Raman spectra in the C–N stretching region (Table 2). I.r. data for some of the tungsten complexes have also been given by Latka.[13] The C–N stretching frequencies show moderate agreement (to 2—4 cm^{-1}), but relatively large disparities are found for the C–NR modes. Our data are reproducible, and the agreement between corresponding molybdenum and tungsten complexes is reassuring.

The spectra are remarkably simple. In the majority of cases the i.r. spectra consist of a single band attributable to C–N stretching and a further, more intense band at higher frequency, assigned to the C–NR stretching modes, accompanied in each case by appropriate isotope bands. In four cases (R = Me or Et) the C–NR band is split by 10—20 cm^{-1}, and in two cases (R = CPh_3) the C–N band is split by 6—7 cm^{-1}. In all cases, solution spectra (benzene, chloroform or ethanol) show a single, sharp band in each region (plus isotope bands), but occasionally a high-frequency shoulder is discernible on the C–NR band. The Raman spectra of the solid complexes show one C–N band (two for R = CPh_3) and two bands in the C–NR region. The correspondences between the i.r. and Raman bands are presumably genuine coincidences. The frequencies do not match exactly but are very close, as graphical comparison clearly demonstrates (see Figure). No rational assignment seems possible if coincidence is not assumed. The complexes thus show one resolved C–N stretching mode (the doublet observed for R = CPh_3 collapses when the complexes are dissolved), and two resolved C–NR stretching modes.

The numbers of bands observed are in all cases less than those expected for any of the possible structures. A high symmetry would seem to be indicated, but the spectra are simpler even than expected for cubic co-ordination (T_d symmetry). Strong coupling between the two sets of vibrations may well occur but this would affect only the positions and intensities of the bands, and not their number. It is unlikely that a Raman band in the C–N region would be weakened sufficiently to escape detection. A cubic configuration might be forced by the largest R-groups but this would require that these d^2-complexes be paramagnetic. All the complexes appear to be diamagnetic, either by direct Gouy measurement, by the observation of sharp n.m.r. signals, or by the absence of e.s.r. signals. Structures of symmetry lower than T_d would be expected to give rise to more complex vibrational spectra.



Schematic representation of the spectra of $W(CN)_4(CNR)_4$; —— i.r., solid; · · · · i.r., $CHCl_3$ solution; – – – – Raman, solid; intensities are normalised to that of the strongest band in each spectrum

In order to resolve this problem, an *X*-ray crystal structure determination was kindly carried out by Dr. F. Cano on the complex $Mo(CN)_4(CNMe)_4$, with which the corresponding tungsten complex is isomorphous.[16] The results unambiguously demonstrate a normal dodecahedral MA_4B_4 structure with the CNMe groups occupying the B-positions. The shape parameters[4] of the co-ordination polyhedron are similar to those of other dodecahedral complexes, and give no reason to expect an unusually simple vibrational spectrum. It is, however, noticeable that only the methyl (and ethyl) compounds give any appreciable splitting of the C–NR stretching modes, although only single Raman bands

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[14] F. Bonati and G. Minghetti, *Inorg. Chem.*, 1970, **9**, 2642; D. F. Lewis and S. J. Lippard, *ibid.*, 1972, **11**, 621.

[15] L. P. Hartley and H. M. Powell, *J. Chem. Soc.*, 1933, 101.

[16] F. Cano and D. W. J. Cruickshank, *Chem. Comm.*, 1971, 1617.

(of intermediate frequency) are observed. Presumably the other complexes have similar dodecahedral structures.

The vibrational spectra can only be explained on the assumption that several of the expected bands are accidentally degenerate. If the dodecahedron is derived by distorting a cubic structure of T_d symmetry, the stretching modes expected are those corresponding to the A_1 and T_2 modes. It seems that the expected splitting of the T_2 mode (into B_2 and E modes) does not occur for the stretching of the C–NR bonds (except for the methyl and ethyl derivatives), although the A_1 mode remains distinct. For the C–N bonds, all three modes must accidentally coincide. Similar effects are reported for the tetrahedral complexes $M(CN)_4^{n-}$, where the A_1 and T_2 modes are very close (3—5 cm^{-1}) for copper and silver ($n = 3$) and are unresolvable for the zinc, cadmium, and mercury complexes ($n = 2$).[17]

Some of the overlapping of bands for the isonitrile complexes could be due to coupling between the two sets of vibrations, which have the same symmetry. Coupling would result in an increased energy separation between corresponding modes of the two sets. That is, relative to their positions in the absence of coupling, the higher-frequency mode would have an increased frequency and the lower-frequency mode would move to still lower frequency. Normally, the A_1 modes have higher frequency than the B_2,E modes. Thus, if coupling between the A_1 modes were stronger than that between the B_2,E modes, the A_1(C–NR) band would move to higher frequency, away from the B_2,E(C–NR) bands, while the A_1(C–N) band would approach and overlap the B_2,E(C–N) bands.

Coupling cannot explain the overlapping of the B_2 and E modes, which must be accidentally degenerate. The complexes thus display ' pseudo-cubic ' behaviour, as far as their vibrational spectra are concerned. A similar effect has recently been demonstrated by Beattie and Gall,[18] who showed that an Si–O–Si system may have ' pseudo-linear ' vibrational characteristics even when the bond angle is 40 or 50° away from linearity. In the complex $Mo(CN)_4(CNMe)_4$, the C–Mo–C bond angles, θ_A and θ_B, are 70·8 and 150·4, compared to 109·5° for the cube. In complexes with large R-groups, θ_B could well be closer to the cube angle. It is curious, however, that the complexes $M(CN)_8^{4-}$, for which the corresponding angles are 70·0 and 145·8°, give well-resolved spectra in which all the expected bands can be recognised.[1,6,19]

It has been suggested that complexes of the type MA_4B_4 should adopt the dodecahedral configuration and that the better π-bonding ligands should occupy the B-sites.[20] In the present case, the isonitrile ligand is the better π-acceptor, and is found in these positions (significant π-donation from the ligands cannot occur in these d^2-complexes). However, the values of the stretching frequencies suggest that the ligands function primarily as σ-donors. Thus the C–NR stretching frequencies are *ca.* 70 cm^{-1} higher than for the free ligands; the C–N frequencies are higher even than for the $M(CN)_8^{4-}$ ions and are comparable to those for the $M(CN)_8^{3-}$ ions. In the latter case, e.s.r. data suggest that the unpaired electron is only slightly delocalised on to the CN-groups.[21] It is possible that a small degree of π-bonding to the isonitrile ligands is sufficient to favour the B-positions.

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[17] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, 1960, **33**, 736.

[18] I. R. Beattie and M. J. Gall, *J. Chem. Soc.* (*A*), 1971, 3569.

[19] S. F. A. Kettle and R. V. Parish, *Spectrochim. Acta*, 1965, **21**, 1087; R. V. Parish, *ibid.*, 1966, **22**, 1191.

[20] L. E. Orgel, *J. Inorg. Nuclear Chem.*, 1960, **14**, 136.

[21] S. I. Weissman and M. Cohen, *J. Chem. Phys.*, 1957, **27**, 1440.