Recent work[25] has shown that a similar relationship exists for the stretching modes of MCl_4 and MBr_4 molecules (M = C, Si, Ge, or Sn). For these species, ν_1 and ν_3 are found to be dependent upon the ionic character of the M–X bond, but here again the nature of the relationship depends on the set of electronegativity values which are used. There seems to be little profit in discussing the detailed nature of such dependences at this point.

Wharf and Shriver[21] noted an interesting effect of oxidation state in their work, which covered both tin(II) and -(IV) halide complexes. They defined a parameter Ω = oxidation state/coordination number and showed that Ω is proportional to f_r in tin–chloride complexes, in which the ratio of the stretching force constants for SnX_3^- to SnX_4 varies from 0.48 to 0.59, with an average value of 0.54 which is in good agreement with the ratio $\Omega(SnX_3^-)/\Omega(SnX_4) = 0.67$. We have tested this suggestion for our compounds and find that the ratio of the stretching force constants for pairs of InX_3^{2-} and InX_4^- anions varies from 0.41 to 0.52, with an average value of 0.46, which is somewhat closer to the ratio $\Omega(InX_3^{2-})/\Omega(InX_4^-) = 0.44$ than is the case for the analogous ratios for the tin compounds. Unfortunately the dependence of f_r on Ω does not hold within the group of indium(III) halide complexes, in which the coordination number varies from four to six. The relevant values are

	Ω	$10^5 f_r$, dyn cm^{-1}
$InCl_4^-$	0.75	1.865
$InCl_5^{2-}$	0.60	1.378, 1.305
$InCl_6^{3-}$	0.50	0.949

Despite this absence of a proportionality between Ω and f_r for these three species, a relatively simple relationship does exist, as is shown by the plot of f_r against coordination number (Figure 1). Again it is difficult to place any detailed interpretation on these relationships, except that an ionic model would require a gradual weakening of bonds with increasing coordination number.

Figure 2 shows another relationship between the log of the primary stretching force constants for the isoelectronic species InX_3^{2-}, SnX_3^-, and SbX_3[26,27] and the oxidation state of the central element. There is some uncertainty in the point for $SbBr_3$, arising from the range of values reported[25] for f_r ($1.338–1.686 \times 10^{-5}$ dyn cm^{-1}). Relationships between stretching frequencies and oxidation state are well-known (see, for example, Adams[28]), but Figure 2 implies the existence of a more precise dependence than is usually acknowledged.

In summary, then, the primary stretching frequencies of the indium(I) and -(III) anionic halide complexes depend on ligand electronegativity, coordination state, and oxidation state in a manner which is qualitatively in keeping with a model of significantly ionic In–X bonding, the details of which remain to be elucidated.

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Reactions of Halocarbonyls of Group VIb Elements. I. Complexes of Tervalent Molybdenum with Nitrogen, Oxygen, and Sulfur Donors

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Preparation of complexes of the type MoX_3L_3 [X = Cl, Br; L = pyridine, nitrile, tetrahydrofuran, tetrahydrothiophene] from the reaction of $Mo(CO)_4X_2$ with the pure liquid donor is described. The results indicate that donor ligands which do not have a special ability to stabilize low oxidation states cause a disproportionation of Mo(II) into Mo(0) and Mo(III). Magnetic properties and infrared and electronic spectral data of the complexes are discussed.

When $Mo(CO)_4Cl_2$ and $Mo(CO)_4Br_2$ are treated with substances containing N, P, As, and Sb as donor atoms, products of the type $Mo(CO)_3L_2X_2$ may be formed.[1–3] Excess pyridine, 2,2′-bipyridine, and 1,10-phenanthroline give complexes of the type $Mo(CO)_2L_2X_2$.[4] These reactions were carried out by dissolving the reactants in a suitable solvent. We were interested to learn whether the use of neat liquid donors would lead to more highly substituted products. Such was found to be the case with trimethyl phosphite which gave $Mo(CO)_2[(CH_3O)_3P]_3X_2$ During the course of this work, Bonati and Mighetti showed that molybdenum halocarbonyls react with excess isocyanides to give complexes with the formulation MoL_5X_2.[5] We have found that reaction of the halocarbonyls with pure $AsEt_3$ in excess gave a photosensitive product of the approximate composition $Mo(CO)_3(AsEt_3)Cl_2$. This is surprising because $AsPh_3$ gives $Mo(CO)_3(AsPh_3)_2Cl_2$.[2]

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TABLE I

COMPLEXES OF TERVALENT MOLYBDENUM PREPARED FROM HALOCARBONYLS

		% found					% calcd				
No.	Compd	Mo	X (Cl or Br)	C	H	Other (N, O, or S)	Mo	X (Cl or or Br)	C	H	Other (N, O, or S)
I	$MoCl_3(NCPh)_3$	18.76	20.74	49.31	3.18	6.93	18.75	20.80	49.28	2.95	6.52
II	$MoCl_3(NCCH_3)_3$	29.35	32.35				29.51	32.69			
III	$MoCl_3(NCCH_3)_4$	26.13	29.06	25.96	3.47	15.23	26.18	29.02	26.22	3.30	15.29
IV	$MoCl_3(NCCH_2Ph)_3$	17.18	19.03	52.82	3.80	7.48	17.21	19.06	52.06	3.82	7.59
V	$MoCl_3(NCCH_2CH_3)_3$	26.01	28.97	29.19	3.99	11.27	26.11	28.94	29.40	4.09	11.43
VI	$MoCl_3[NC(CH_2)_2CH_3]_3$	23.41	26.05	35.54	5.34	10.36	23.43	25.99	35.19	5.19	10.26
VII	$MoCl_3[NCCH(CH_3)_2]_3$	23.12	26.01	35.30	5.29	10.13	23.43	25.99	35.19	5.19	10.26
VIII	$MoCl_3[NC(CH_2)_3CH_3]_3$	20.95	23.40	39.81	5.87	9.22	21.24	23.55	39.81	6.03	9.31
IX	$MoBr_3(NCPh)_3$	14.81	35.00	39.68	3.03	6.10	14.87	37.06	39.10	2.34	6.51
X	$MoBr_3(NCCH_3)_3$	20.45	51.73	15.47	2.60	8.91	20.91	52.25	15.71	1.98	9.16
XI	$MoBr_3(NCCH_3)_4$	19.18	47.78	18.38	2.35	10.04	19.19	47.96	19.22	2.42	11.21
XII	$MoBr_3(NCCH_2Ph)_3$	13.71	34.65	43.54	3.32	6.04	13.96	34.89	41.95	3.08	6.12
XIII	$MoBr_3(NCCH_2CH_3)_3$	19.21	47.64	19.54	3.06	8.44	19.15	47.87	21.58	3.02	8.39
XIV	$MoBr_3[NC(CH_2)_2CH_3]_3$	17.54	44.20	26.81	3.54	7.85	17.67	44.50	26.54	3.90	7.74
XV	$MoBr_3[NCCH(CH_3)_2]_3$	17.50	44.22	26.68	3.81	7.91	17.67	44.50	26.54	3.90	7.74
XVI	$MoBr_3[NC(CH_2)_3CH_3]_3$	16.40	40.96	30.89	4.40	7.37	16.40	40.99	30.79	4.65	7.18
XVII	$MoCl_3(C_5H_5N)_3$	21.13	24.08	41.29	3.48	9.50	21.82	24.20	40.98	3.44	9.56
XVIII	$MoCl_3(C_5H_5N)_4$	18.58	20.77				18.49	20.51			
XIX	$MoBr_3(C_5H_5N)_3$	16.71	41.78	31.37	2.81	7.47	16.74	41.84	31.44	2.64	7.33
XX	$MoCl_3(C_4H_8O)_3$	23.33	25.30	34.28	5.84	11.21	22.97	25.41	34.43	5.78	11.47
XXI	$MoCl_3(C_4H_8S)_3$	20.0	22.38	31.08	5.34	20.22	20.55	22.79	30.90	5.28	20.61
XXII	$MoBr_3(C_4H_8O)_3$	17.20	43.39	25.95	4.38	8.58	17.38	43.43	26.11	4.38	8.70
XXIII	$MoBr_3(C_4H_8S)_3$	16.70	39.94	23.88	4.08	16.14	16.00	39.94	24.01	4.03	16.03

When $Mo(CO)_4Cl_2$ was treated with pure liquid acetonitrile or benzonitrile, tervalent molybdenum complexes, $MoCl_3L_3$, were isolated as the major product. Because nitrile complexes of Mo(III) are useful starting materials for preparing other Mo(III) complexes[6] and products were obtained relatively easily in comparison with previous methods,[6-8] our observation led us to investigate the reaction of other nitriles with $Mo(CO)_4X_2$. We have also studied the reactions with pyridine, tetrahydrofuran, and tetrahydrothiophene and in all cases the major product was of the type MoX_3L_3. Dimethyl sulfoxide reacted similarly but the product was not isolated in a pure form.

The evidence suggested that ligands such as nitrile, which have no special ability to stabilize low oxidation states, react with disproportionation of the Mo(II) to give complexes of Mo(0) and Mo(III). On the other hand, phosphines, arsines, etc., have the capacity to preserve the divalent state of the metal during reaction. The behavior of tungsten was slightly different. When $W(CO)_4Cl_2$ was treated with pyridine, rapid disproportionation occurred only upon heating and then the initial products were $WCl_4(py)_2$ and complexes of W(0). The tetravalent tungsten compound was subsequently reduced to $WCl_3(py)_3$ upon raising the temperature to 140°. When $W(CO)_4X_2$ was heated with benzonitrile, the major product had the empirical composition WX_2L_2 which we believe to be a cluster compound. Details of the work with tungsten compounds will be given in a future publication.

Experimental Section

Materials.—Chlorine (Matheson) was dried by passing through concentrated sulfuric acid and then over a 1 m long bed of P_4O_{10}. Bromine (BDH) was freshly distilled before use. Molybdenum hexacarbonyl (Alfa or K & K) was finely powdered in a blender and kept over P_4O_{10} in a desiccator for 12 hr before use. Benzonitrile and phenylacetonitrile were distilled from calcium oxide. Other nitriles (Eastman, Aldrich, or BDH) were purified by distilling from P_4O_{10}, kept over molecular sieves, and vacuum distilled prior to use. Tetrahydrofuran (Fisher) and tetrahydrothiophene (Baker) were distilled from lithium aluminum hydride. Pyridine (BDH) was distilled from calcium oxide.

Preparations. Halocarbonyls.—Molybdenum chlorocarbonyl was prepared according to a literature method.[1] The published procedure for preparing the bromocarbonyl[2] was modified in that the product was crystallized by only partially evaporating the solvent and it was isolated by filtering the cooled mixture. The product so obtained was a pure orange color.

Molybdenum(III) Complexes.—Molybdenum halocarbonyl (2–5 g) was put into a reaction vessel which had been thoroughly dried under vacuum and then filled with dry oxygen-free nitrogen. The liquid donor compound (15–25 ml) was added and the mixture stirred. The resulting yellow-brown[9a] solution was rapidly filtered in an apparatus described by Fritz, *et al.*[9b] As stirring of the filtrates continued, precipitates of the following colors appeared: nitriles and pyridine, yellow; tetrahydrofuran, pink; tetrahydrothiophene, orange. With chloro complexes, precipitates formed within a few minutes, but for the bromo complexes, periods of from 0.5 to 5 hr were required for precipitation to commence. At least 24 hr was allowed for reaction to go to completion. Chloro complexes were separated directly by filtration. In the case of the more soluble bromo complexes, the solution was concentrated by pumping off some of the excess donor liquid when possible and then filtered. The separated complexes were washed with a few milliliters of donor–ether mixture (1:5) and finally with several portions of ether. The products were dried *in vacuo* at room temperature and stored in nitrogen-filled ampoules. Analyses are given in Table I.

Partially Substituted Halocarbonyls.—$[Mo(CO)_4Cl_2]_2$ (4.4 g) was suspended in ether (30 ml) and acetonitrile (1.30 g) in ether (20 ml) was added. The mixture was stirred for 12 hr and filtered, and the dull green solid was washed with several portions of ether. An ir spectrum of the product showed bands characteristic of nitrile and carbonyl ligands. Chlorine and molybdenum analyses showed that the product was probably $Mo(CO)_3(NCCH_3)Cl_2$, but as it decomposed gradually, it was not possible to obtain reliable commercial analyses of the remaining elements. *Anal.* Calcd for $C_5Cl_2H_3MoNO_3$: C, 20.57; H, 1.04; Cl, 24.3; Mo, 32.9. Found: C, 19.31; H, 2.75; Cl, 25.4; Mo, 32.6. The pyridine complex $Mo(CO)_2(py)_2Cl_2$ was prepared according to the procedure of Colton and Rix.[4] *Anal.* Calcd for $C_{12}H_{10}Cl_2MoN_2O_2$: C, 37.82; H, 2.65;

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(7) P. W. Smith and A. G. Wedd, *J. Chem. Soc. A*, 231 (1966).

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(9) (a) The solution of $Mo(CO)_4Cl_2$ in THF rapidly turned green. (b) G. Fritz, D. Habel, D. Kummer, and G. Teichman, *Z. Anorg. Allg. Chem.*, **302**, 60 (1959).

Cl, 18.61; Mo, 25.18; N, 7.35; O, 8.40. Found: C, 37.87; H, 2.99; Cl, 18.82; Mo, 24.5; N, 7.24; O, 8.39.

Reactions of Partially Substituted Halocarbonyls with Excess Pure Donor Compound.—$Mo(CO)_3(NCCH_3)Cl_2$ (3 g) was stirred with acetonitrile (25 ml) during which operation the solution color slowly changed from violet to yellow. In 12 hr yellow crystals had formed. Stirring was continued for a further 12 hr and the solid product was separated by filtration, washed with acetonitrile followed by ether, and dried in a current of nitrogen. Analysis showed the compound to be $MoCl_3 \cdot 4NCCH_3$ (compound III in Table I). When dried under vacuum, the product had the formula $MoCl_3 \cdot 3NCCH_3$. The filtrate was evaporated to dryness on a water bath and the dull yellow solid was leached with petroleum ether (bp 30–60°). Upon concentrating this extract, white crystals were recovered. These gave an ir spectrum identical with that of $Mo(CO)_6$. The crystals were somewhat volatile, further indicating that they were $Mo(CO)_6$.

$Mo(CO)_2(py)_2Cl_2$ (3 g) was treated with excess pyridine (20 ml) and the mixture stirred for 24 hr. During this time the orange suspended solid was replaced by a yellow solid. Analysis showed that it was $Mo(py)_3Cl_3$. The filtrate was treated with dilute H_2SO_4 and a steam distillation of the resulting solution produced a white solid with an ir spectrum identical with that of $Mo(CO)_6$.

Analyses.—Samples were prepared for determination of metal and halogen by fusion in a Parr bomb with Na_2O_2 and lactose. The melt was dissolved in water and filtered. Molybdenum was determined gravimetrically as lead molybdate[10,11] in the presence of ammonium acetate. Halogen was determined either gravimetrically or potentiometrically with $AgNO_3$. Precipitation of Ag_2MoO_4 did not occur if the samples were made sufficiently acidic. Carbon, hydrogen, oxygen, sulfur, and nitrogen were determined by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany.

Infrared Spectra.—Nujol mulls were used to obtain spectra in the region 4000–600 cm^{-1}. For spectra in the range 600–250 cm^{-1}, pressed cesium iodide disks were employed. The spectrometer used was a Beckman Model IR-20.

Electronic Spectra.—Complexes were dissolved in the liquid donor and the spectra recorded with a Beckman Model DK-2 spectrophotometer. Concentration studies indicated that hydrolysis due to possible residues of water in the solvents had a negligible influence.

Magnetic Measurements.—Magnetic susceptibilities were determined at room temperature with a Gouy balance which had a maximum field strength of 5200 Oe. Diamagnetic corrections were obtained where possible from standard compilations.[12,13] Otherwise, diamagnetic corrections were obtained by use of Pascal's constants.

Results and Discussion

With the exception of two acetonitrile complexes and a pyridine complex, all of the Mo(III) compounds which were isolated had the general formula MoX_3L_3. The exceptions mentioned crystallized as MoX_3L_4 and were recovered as such if the crystals were dried at room temperature in a current of nitrogen. $MoCl_3(NCCH_3)_4$ is known to be nonionized in acetonitrile.[7] The pyridine complex $MoCl_3(py)_4$ was essentially a nonconductor in pyridine and nitrobenzene. On the other hand, a 5.7×10^{-4} *M* solution of $MoBr_3(NCCH_3)_4$ in acetonitrile had a molar conductance of 40.7 $ohm^{-1}\ cm^2$ at 25°. This is low compared to typical values for a 1:1 electrolyte (~160 $ohm^{-1}\ cm^2$). In all cases of the 1:4 adducts, one donor molecule was removed by heating the compound *in vacuo* at 30–40°. At 50°, $MoCl_3(NCCH_3)_3$ decomposed further to give $MoCl_3 \cdot xNCCH_3$ where $2 < x < 3$. The bromo analog did not decompose under these conditions.

When formed initially, the precipitates were contaminated with carbonyl-containing impurities which gave absorptions in the ranges 1950–1980 and 2020–2040 cm^{-1}. Molybdenum hexacarbonyl collected on the walls of the upper part of the reaction vessel. These observations suggest that partially substituted products of the type $Mo(CO)_xL_yX_2$ were formed initially and these, upon further reaction with the donor liquid, underwent disproportionation to compounds of Mo(0) and Mo(III). Partially substituted carbonyls such as $Mo(CO)_2(py)_2Cl_2$, when treated with the liquid donor, gave $Mo(CO)_6$ and the Mo(III) complex. In one case, the mother liquor was shown to contain soluble yellow carbonyl complexes of molybdenum which contained no halogen. The ir spectra of these substances suggested that they were mixtures of the compounds $Mo(CO)_n(NCCH_3)_{6-n}$.[14] This reaction shows that the disproportionation of Mo(II) probably occurs after the formation of the partially substituted carbonyl halide. Disproportionation of this sort is known to occur with other carbonyl-containing systems when the added ligand cannot sustain an unusually low oxidation state, *e.g.*

$$Fe(CO)_5 + \text{amine} \longrightarrow [Fe(\text{amine})_6]^{2+}[Fe(CO)_4]^{2-}$$

The Mo(III) complexes are all paramagnetic, most of them with moments in the range 3.7–3.9 BM. A few, notably those containing oxygen or sulfur, had moments as low as 3.4 BM. Such values are reasonable for quasioctahedral complexes containing a $4d^3$ ion. The moment of a strictly octahedral complex should be given by

$$\mu_{\text{eff}} = 2(1 - 4\lambda/10Dq)[S(S+1)]^{1/2}$$

where λ is the spin–orbit coupling parameter. As λ for Mo(III) is *ca.* 240 cm^{-1} (free ion value)[15] and $10Dq$ is of the order of 20,000 cm^{-1} (*cf.* the value given for $MoCl_6^{3-}$ ion[16]), a value of $\mu_{\text{eff}} = 3.70$ BM is expected.

TABLE II

CARBON–NITROGEN STRETCHING FREQUENCIES (CM^{-1}) OF NITRILE COMPLEXES OF Mo(III)

Compd no.	C–N str freq in coordinated nitrile	C–N str freq in uncoordinated nitrile	Diff
I	2238	2228	10
III	2275, 2255[a]	2253	22, 2[a]
IV	2275	2244	31
V	2268	2243	25
VI	2273	2243	30
VII	2273	2252	21
VIII	2277	2242	35
IX	2238	2228	10
XI	2277, 2257[a]	2253	24, 4[a]
XII	2275	2244	31
XIII	2268	2243	25
XIV	2268	2243	25
XV	2263, 2270	2252	
XVI	2277	2242	35

[a] One of the four nitrile groups is apparently not coordinated strongly.

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(16) C. Furlani and O. Piovesana, *Mol. Phys.*, **9**, 341 (1965).

Values closer to the spin-only value of 3.87 are expected if the ligand field is significantly distorted.

Spectra.—It is seen from Table II that the C–N stretching frequency of the nitriles increases upon coordination by 10–30 cm^{-1}. Such an increase has been observed in many nitrile complexes.[17] It is difficult to assign the metal–ligand frequencies in these compounds. Other infrared bands are listed in Table III. Bands at or near 320 and 305 cm^{-1} in the chloro complexes containing nitrile were attributed to Mo–Cl stretching as these were intense bands which were absent from the bromo analogs. The chloro complexes generally gave an additional weak band in the range 280–295 cm^{-1} which was also absent from the bromo complexes. We believe that this also is caused by Mo–Cl stretching but the assignment is uncertain as there are other weak bands in this region. It is possible that bands due to metal–nitrogen stretching may appear although in certain complexes they have been found at fairly low energies.[18] The free nitriles show weak absorption in this region as well.[19] The appearance of three Mo–Cl stretching modes suggests that the compounds have the meridional (trans) configuration, but as the infrared data provide only uncertain evidence, discussion of further structural information may be in order.

TABLE III

INFRARED ABSORPTION FREQUENCIES IN THE REGION 600–250 CM^{-1}

Compd no.	Absorption bands, cm^{-1}
I	548 s, 460 sh, 395 w, 340 m, 320 s, 305 m, 295 sh, 282 w, 270 sh
II	560 w, 480 sh, 415 w, 390 w, 319 s, 299 m, 287 w, 275 w, 263 w
IV	570 sh, 540 s, 460 m, 444 m, 395 w, 320 s, 305 m, 295 m, 287 w, 270 w
V	565 w, 460 m, 445 s, 395 w, 355 sh, 320 s, 305 m, 295 sh, 285 w, 270 w
VI	565 w, 480 sh, 420 m, 320 s, 305 m, 295 sh, 280 w, 270 sh
VII	560 w, 480 w, 450 w, 370 w, 335 s, 320 s, 303 s, 295 w, 280 w, 270 w
VIII	540 w, 450 w, 410 m, 340 sh, (320–305 br), 280 w, 270 sh, 262 w
IX	548 s, 450 sh, 390 w, 335 w, (310–285 br), 270 m
X	560 m, 412 m, 305 w, 290 br, 270 br
XII	447 s, 395 w, 365 w, 265 m
XIII	556 m, 480 w, 455 w, 410 w, 373 w, 335 sh, 310 sh, 290 w, 270 s
XIV	570 w, 450 w, 410 w, 375 m, 309 sh, 287 sh, 268 s
XV	580 sh, 570 w, 550 m, 480 m, 375 w, 335 br, 290 br
XVI	410 w, 270 m, 255 w
XVII	555 w, 438 m, 340 sh, 318 vs, 290 sh, 278 m
XIX	438 m, 264 s, br
XX	360 sh, 331 s, 313 s, 264 w
XXI	516 s, 474 w, 334 s, 310 s, 289 m, 270 w
XXII	575 w, 380 sh, 270 br
XXIII	510 s, 470 w, 306 sh, 280 sh, 256 s

The electronic spectra (Table IV) show features of special interest. Following Furlani and Piovesana,[16] who studied the ions $MoCl_6^{3-}$ and $MoBr_6^{3-}$, we relate the bands near 8000, 14,000, 20,000, and 24,000 cm^{-1} to the transitions $^4A_{2g} \rightarrow {}^2E_g$, $^2T_{1g}$, $^4A_{2g} \rightarrow {}^2T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{2g}$, and $^4A_{2g} \rightarrow {}^4T_{1g}$ of an equivalent octahedral complex. Jørgensen has proposed the same assignment for $MoCl_6^{3-}$,[20] and this scheme has been followed also by Smith and Wedd.[8]

TABLE IV

ABSORPTION BANDS IN THE ELECTRONIC SPECTRA OF Mo(III) COMPLEXES IN SOLUTION[a]

Compd no.	Freq × 10^{-3}, cm^{-1}
IV	13.5, 14.3, 15.9, 27
V	14, 22 sh, 27.5
VI	13.2, 14.1, 15.9, 22 sh, 27
VIII	14.3, 19.3, 27.3
XII	6.8 br, 8.0, 8.5, 12.8, 13.7, 16.9, 20.8 sh, 28
XIII	7.0 br, 8.0, 8.5, 12.8, 13.8, 15, 20.8 sh, 24, 26.5 sh
XIV	6.8 br, 8.0, 8.5, 12.8, 13.4, 15, 20.8 sh, 24.1, 28.2 sh
XVI	6.8 br, 8.0, 8.5, 14, 15.4, 20.8
XX	5.8, 9.9, 12.8, 14.8, 19.4, 24.4 sh, 28.2, 30.4
XXI	5.7, 5.9, 8.5, 12.2, 14.1, 15.4, 17.2, 21.3, 27, 30
XXII	5.8, 9.5, 12.9, 15.8, 19.2, 23.8, 26.3, 31.4
XXIII	5.8, 5.9, 8.4, 9.9, 14, 21, 23.6, 30.1

[a] Compounds were dissolved in pure donor except XXI and XXIII which were dissolved in CH_2Cl_2.

The adducts examined here have lower symmetry, either C_{2v} (meridional configuration) or C_{3v} (facial configuration). In these symmetries, the octahedral states split as follows. (a) $O_h \rightarrow C_{3v}$: $A_{2g} \rightarrow A_2$, $E_g \rightarrow E$, $T_{1g} \rightarrow A_2 + E$, $T_{2g} \rightarrow A_1 + E$. (b) $O_h \rightarrow C_{2v}$: $A_{2g} \rightarrow A_2$, $E_g \rightarrow A_1 + A_2$, $T_{1g} \rightarrow A_2 + B_1 + B_2$, $T_{2g} \rightarrow A_1 + B_1 + B_2$. In addition, Sugano and Tanabe have shown[21] that if spin–orbit coupling is not small, appreciable splitting of the E states in C_{3v} symmetry will occur well. Consequently, the higher energy bands should each consist of three components and the lowest energy band of five components. Because the energies of spin-allowed transitions are strongly dependent upon the instantaneous ligand field strength during a vibration of the molecule, the quartet–quartet transitions are broad and small splittings are not resolved. The spin-forbidden transitions are not strongly field dependent, however;[21] consequently splittings of the doublet states may be seen in the spectra such as those shown in Figure 1.

Smith and Wedd's reflectance spectra of nitrile complexes of Mo(III) failed to reveal the splittings.[8] Allen, *et al.*, reported a pair of bands at 13,400 and 15,100 cm^{-1} in $MoBr_3(PPh_3)_2(NCCH_3)$ which they assigned to $^4A_{2g} \rightarrow {}^2E_g$[6] following Hartmann and Schmidt.[22] As noted above, later workers have reassigned the band near 15,000 cm^{-1} to $^4A_{2g} \rightarrow {}^2T_{2g}$. No reason was given for the doublet character, but the complex has low symmetry.

Our success in observing the splitting of the quartet → doublet transitions is no doubt due to two factors. First, we worked with very concentrated solutions and, second, the extinction coefficients of the d–d transitions are unusually large. This was observed also by Carmichael, *et al.*,[23] in their work with bipyridine complexes of Mo(III). Chloro complexes were insufficiently soluble to give good resolution of the spin-forbidden bands, but in one of them, the butyronitrile complex, the resolution of the $^4A_{2g} \rightarrow {}^2T_{2g}$ band into three components was quite distinct. The bromo complexes, dissolved in their parent nitriles at a

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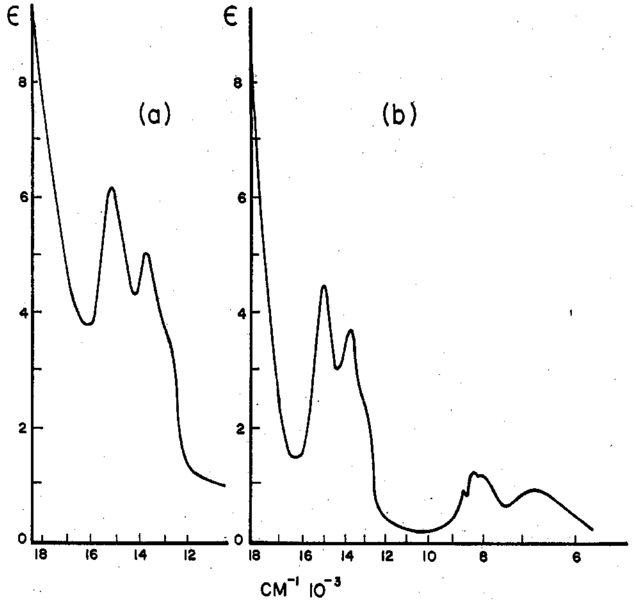

Figure 1.—Spin-forbidden absorption bands in nitrile complexes of Mo(III): (a) XII, 0.059 *M;* (b) XIV, 0.080 *M.* Parent nitrile was used as solvent.

concentration of 8×10^{-2} *M,* showed these three components clearly in all cases except the valeronitrile complex. In this, the weak shoulder on the low-energy side of the set of the bands was not resolved. The $^4A_{2g} \rightarrow {}^2E_g, {}^2T_{1g}$ components were weaker and less well resolved but it appears that there are more than three components.

Absorptions are seen at still higher energies than those discussed above. As these have been discussed already,[8] we shall not comment on them further.

The three spin-forbidden transitions centered near 14,000 cm^{-1} may be compared with the model of Sugano and Tanabe for the C_{3v} configuration. If we postulate this structure, the observed splitting of the E state is too large to be consistent with the magnitude of the spin–orbit coupling parameter for Mo(III) which has been shown[24] from the esr spectrum to be 550 cm^{-1} in $MoCl_6^{3-}$.

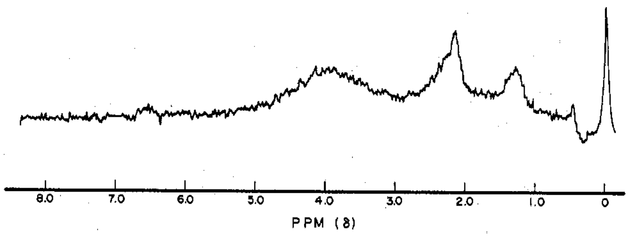

Figure 2.—Proton magnetic resonance spectrum of $MoBr_3(NCCH_2CH_3)_3$.

If the compound $MoCl_3[NC(CH_2)_2CH_3]_3$ had C_{3v} symmetry, the observed transitions at 14,100, 15,900, and 13,200 cm^{-1} would represent transitions to the states designated W_0, W_1, and W_2 by Sugano and Tanabe. From the observed differences in these energies we obtain a spin–orbit coupling parameter, ζ, with the value 1130 cm^{-1}. This is much too high, so we propose that the C_{2v} model is incorrect.

A further kind of evidence that the nitrile complexes have the meridional configuration comes from the nmr spectrum of $MoBr_3(NCCH_2CH_3)_3$. The adducts of Mo(III) are all paramagnetic so that nmr spectra are badly broadened. In the one case mentioned, the spectrum was sufficiently clear to permit an assignment of probable structure. The spectrum is shown in Figure 2. Apart from a spinning side band near the TMS peak, there are unresolved peaks at *ca.* 1.3, 2.2, and 4 ppm downfield from TMS. The intensity ratios are 28:66:67 which is close to 3:6:6. This corresponds to an assignment in a meridional configuration in which the high-field peak is due to a methyl group on the molecular axis and the next peak is due to the two other methyl groups while the methylene protons form one unresolved broad band at the lowest field position. The unique methyl group is practically unshifted relative to TMS from its position in the pure nitrile.

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