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Notes

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Reinterpretation of Five Recent Crystal Structures of Heteropoly and Isopoly Complexes: Divanadododecamolybdophosphate, Trivanadoenneamolybdophosphate, "γ-Dodecatungstophosphate", the Dodecamolybdate–Dodecamolybdomolybdate Blue Complex, and Dihydrogen Decavanadate

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When one of us published in 1971 a review of the heteropoly and isopoly complex molecular structures,[1] 25 crystal structure determinations had appeared, of which only 11 were completely described. Since then some 100 such determinations have been reported, mostly of high quality. This literature, which forms the foundation for our understanding of the chemistry of this class of compounds, is generally not subject to ambiguity or varying interpretations. However, as Marsh and Shoemaker[2] recently showed, occasionally a crystal structure study does fall into errors of procedure and interpretation that can lead to major chemical misunderstanding. We draw attention here to four such flawed studies concerned with isopoly and heteropoly complexes.

Divanadododecamolybdophosphate,[3] $[PV_2Mo_{10}O_{40}]^{5-}$, Trivanadoenneamolybdophosphate,[3] $[PV_3Mo_9O_{40}]^{6-}$, and "γ-Dodecatungstophosphate",[4] $[PW_{12}O_{40}]^{3-}$

All of these tungstate and vanadomolybdate complexes are described as a so-called new complex similar to the Keggin molecule but having higher, octahedral symmetry and more clathrate character, with the PO_4 group in disorder within the molecule. Although the structure of the tungstate complex described is not well refined,[4] it is clear that this molecular structure is virtually identical with that in the vanadomolybdate complexes, which were described in detail.[3] We conclude from internal evidence in the latter report that both consist of an ordinary Keggin molecule in full twofold disorder within the crystal.

Sergienko et al.[3] have reported complete structure determinations of $H_5[PV_2Mo_{10}O_{40}]\cdot 36H_2O$ at 25 and −70 °C and of $H_6[PV_3Mo_9O_{40}]\cdot 30H_2O$ at 25 °C. Both crystals are isostructural in space group $P4/mnc$ (for the latter compound, $a = 12.824$ Å, $c = 18.246$ Å, and $Z = 2$), and the careful structure analyses were carried to conventional R values of 0.068, 0.061, and 0.097, respectively. The site symmetry of the molecule in these crystals is $4/m$, which is incompatible with the tetrahedral symmetry of the Keggin molecule. Sergienko et al. recognized that the central PO_4 group must be disordered, as indicated by the fact that P is surrounded by a cube of O atoms at 1.55–1.58 Å (see Figure 1), with each O site half-occupied. They consider these O atoms not to be associated with the vanadomolybdate cage, which they described as a linkage of square pyramids having overall octahedral symmetry.

Table I

	$[PW_{12}O_{40}]^{3-}$			$[PV_2Mo_{10}O_{40}]^{5-}$		
	x	y	z	x	y	z
P	0	0	0	0	0	0
M	2.51	2.51	0	2.52	2.52	0
O(a)	0.88	0.88	0.88	0.90	0.90	0.90
O(b–c)	3.15	1.30	1.30	3.20	1.33	1.33
O(d)	3.69	3.69	0	3.69	3.69	0

For the $[PV_2Mo_{10}O_{40}]^{5-}$ complex, Sergienko et al. obtained anisotropic thermal parameters for all of the atoms of the molecule but made no attempt to interpret these parameters. We have produced an ORTEP plot of the molecule based on their parameters, which is shown in Figure 1. The most notable feature revealed in this plot is the extreme elongation of the linking O atoms O(2), O(3), and O(6). These three crystallographically different atoms are equivalent in the pseudooctahedral symmetry of the molecule and are all consistently elongated nearly parallel to the molecular threefold symmetry axes. If we now refer to the Keggin molecule itself, as defined by Evans,[1] it is interesting to construct a doubled molecule, with a second Keggin molecule rotated 90° about a $\bar{4}$ axis and superimposed on the first. We find that metal and O atoms appear in pairs separated by less than 0.6 Å. From the accurate dimensions for $[PW_{12}O_{40}]^{3-}$ obtained by Spirlet and Busing[5] for the fully ordered structure of $H_3PW_{12}O_{40}\cdot 21H_2O$ and with the atoms designated according to Evans,[1] the pairs are displaced as follows: W–W, 0.180 Å; O(b)–O(c), 0.582 Å; O(d)–O(d), 0.404 Å. The mean coordinates (in Å; see Table I) of the centers of these pairs are close to the coordinates of the disordered $[PV_2Mo_{10}O_{40}]^{5-}$ complex averaged over octahedral symmetry. The atom pairs are shown in Figure 1b, which bears a striking resemblance to Figure 1a. The pair vector O(b)–O(c) has the coordinates 0.359, 0.324, and 0.324 Å and thus makes an angle of 2.1° to the threefold symmetry axis. The O(2), O(3), and O(6) atoms in Figure 1a are oriented in just that way and have ellipsoid dimensions (in Å) as follows:

	$\bar{u}_1$	$\bar{u}_2$	$\bar{u}_3$	$\angle\bar{u}_3$-3 axis
O(2)	0.16	0.19	0.43	16°
O(3)	0.16	0.20	0.42	8°
O(6)	0.16	0.22	0.42	13°

It is clear that all the atom pairs shown in Figure 1b fall well inside the ellipsoids of Figure 1a.

The conclusion is inescapable that these tetragonal structures contain normal Keggin molecules disordered as a whole in two positions related by a 90° rotation about the molecular $\bar{4}$ axis. This model was originally proposed for these crystals by Sergienko et al.[6] but was later repudiated.[3] Other well-refined structures of vanadomolybdate complexes show the normal Keggin structure, for example, $K_6[V^{IV}V^{V}_2Mo_{10}O_{40}]\cdot 13H_2O$ (blue)[7] and $Na_3H_6[PV_6Mo_6O_{40}]\cdot 16H_2O$.[8]

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(1) Evans, H. T., Jr. In "Perspectives in Structural Chemistry"; Dunitz, J. D., Ibers, J. A., Eds.; Wiley: New York, 1971; pp 1–59

(2) Marsh, R. E.; Shoemaker, V. *Inorg. Chem.* **1979**, *18*, 2331.

(3) Sergienko, V. A.; Porai-Koshits, M. A.; Yurchenko, E. N. *Zh. Strukt. Khim.* **1980**, *21*, 111; *J. Struct. Chem. (Engl. Transl.)* **1980**, *21*, 87.

(4) Fuchs, J.; Thiele, A.; Palm, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *23*, 789; *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *87B*, 1418.

(5) Spirlet, M.-R.; Busing, W. R. *Acta Crystallogr., Sect. B* **1978**, *B34*, 907.

(6) Sergienko, V. S.; Porai-Koshits, M. A.; Fedotov, M. A.; Yurchenko, E. N.; Kusnetsova, L. I. *Zh. Strukt. Khim.* **1977**, *18*, 976; *J. Struct. Chem. (Engl. Transl.)* **1977**, *18*, 776.

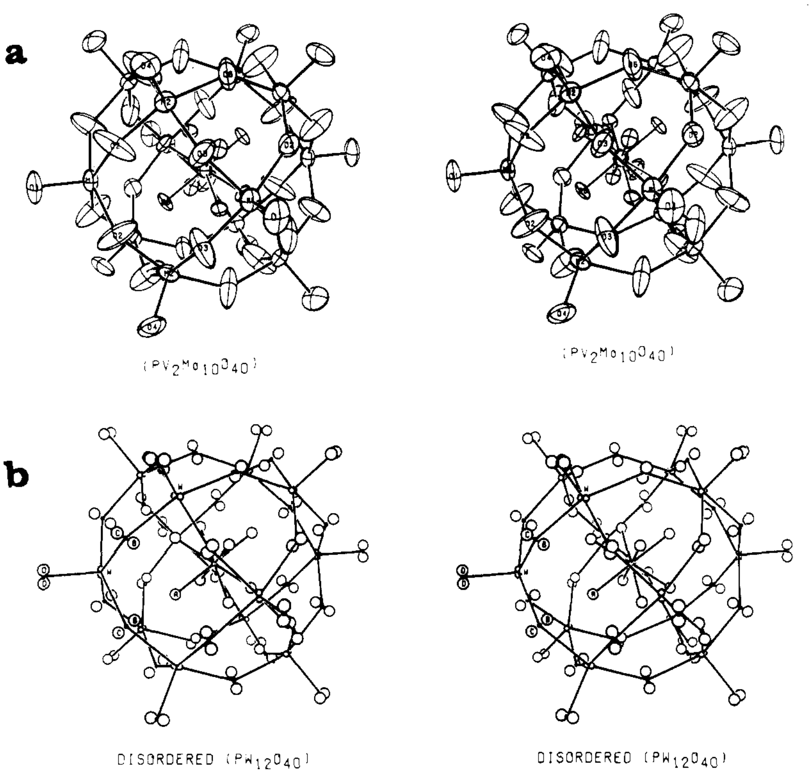

Figure 1. Stereoscopic views of (a) $[PV_2Mo_{10}O_{40}]^{5-}$ as determined by Sergienko et al.[3] (ellipsoids enclose atoms with 50% probability) and (b) $[PW_{12}O_{40}]^{3-}$ twinned by 90° rotation about the $\bar{4}$ axis and self-superimposed. In (b), pseudobonds are drawn between atom-pair midpoints to simulate the configuration in (a).

The small displacement of the terminal O atoms O(d) in the two disordered positions (0.40 Å) shows that the Keggin molecule should pack in a crystal nearly equally well in either position, and disorder should be expected more often. The recent description[4] of a $[PW_{12}O_{40}]^{3-}$ molecule nearly identical with that proposed by Sergienko et al.[3] must actually represent this same disorder, that is, of the entire Keggin molecule, not just the PO_4 group. Fuchs et al.,[4] who were apparently unaware of the work of Sergienko et al.,[3] proposed an octahedral model for the phosphotungstate molecules in the compound $[N(C_4H_9)_4]_4[PW_{12}O_{40}]$ in a crystal with space group $P\bar{1}$ ($Z = 2$). Although their structure cannot be examined in detail because the O positions are left with ±0.08 Å uncertainty, the W–W distances average 3.56 Å, comparable to 3.55 Å in the disordered PW_{12} model defined above. (Individual W–W distances calculated from their published coordinates range irregularly from 3.38 to 3.74 Å.) We maintain that their "γ-$[PW_{12}O_{40}]^{3-}$" does not exist and merely represents an α-$[PW_{12}O_{40}]^{3-}$ Keggin-type molecule in twofold disorder about the molecular $\bar{4}$ axis. The γ notation is particularly unfortunate here because the symbols α, β, γ, δ, and ϵ serve conveniently to denote the various isomers of the Keggin molecule involving different linkage combinations of the four octahedral W_3O_{13} triple groups.[9–11]

Dodecamolybdate–Dodecamolybdomolybdate,[12] $[H_4Mo_{12}O_{40}]^{4-}{}_{0.67}[Mo^tMo_{12}O_{40}]^{4-}{}_{0.33}$

This unusual blue complex (two extra electrons are said to reside in the Mo_{13} moiety) was described by Yamase et al.[12] as occurring in tetragonal crystals with space group $I\bar{4}$ (a = 14.908 Å, c = 10.323 Å, Z = 2). Their structure analysis reached R = 0.037. There is only one crystallographically distinct molecule in the unit cell, but Yamase et al. unexpectedly found appreciable density at the origin. They found that this density could be accounted for by assuming that the site is occupied one-third of the time by Mo in tetrahedral coordination (Mo^t). We believe that this central atom must be Si, which has just one-third the number of electrons that Mo has. This alternative interpretation was also suggested previously by Spitsyn et al.[13]

The most telling clue leading to this conclusion lies in the central tetrahedral bond length, which is reported to be 1.628 (7) Å. Gatehouse and Leverett,[14] in their structure study of K_2MoO_4, found an Mo–O bond length of 1.76 (1) Å. They surveyed six previously studied orthomolybdate structures and found that the tetrahedral distance never deviated more than 0.006 Å from the average value of 1.767 Å. The Si–O bond in isolated silicate structures shows more variation, in the range 1.61–1.66 Å, but the average value is close to 1.63 Å. In olivines, $[(Mg,Fe)_2SiO_4]$, the Si–O bond length ranges from 1.619 to 1.653 Å and averages 1.637 Å;[15] in zircon ($ZrSiO_4$), the single length is 1.622 (1) Å;[16] and in $(CN_3H_6)_4[SiMo_{12}O_{40}]\cdot H_2O$, the average Si–O bond length is 1.639 Å, ranging from 1.627 to 1.641 Å.[17] The comparison with the tetrahedral distance determined by Yamase et al. is compelling. The scattering curve for Si is very close to that of $^1/_3$Mo as shown in Figure 2 and would allow an equally satisfactory refinement. Dr. T. Yamase has kindly replied to our inquiry about his

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(7) Björnberg, A.; Hedman, B. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1018.

(8) Klevtsova, R. F.; Yurchenko, E. N.; Glinskaya, L. A.; Detusheva, L. G.; Kutsnetsova, L. J. *Zh. Strukt. Khim.* **1981**, *22*, 49; *J. Struct. Chem.* (*Engl. Transl.*) **1981**, *22*, 840.

(9) Baker, L. C.; Figgis, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3794.

(10) Matsumoto, K. Y.; Kobayashi, A.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3146.

(11) Pope, M. T. "Heteropoly and Isopoly Metallates"; Springer-Verlag: New York, 1983.

(12) Yamase, T.; Ikawa, T.; Ohashi, Y.; Sasada, Y. *J. Chem. Soc., Chem. Commun.* **1979**, 697.

(13) Spitsyn, V. J.; Kazanskii, L. P.; Torchenkova, E. A. *Sov. Sci. Rev., Sect. B* **1981**, *3*, 111.

(14) Gatehouse, B. M.; Leverett, P. *J. Chem. Soc. A* **1969**, 1968.

(15) Brown, G. E.; Prewitt, C. T. *Am. Mineral.* 1973, *58*, 577.

(16) Robinson, K.; Gibbs, G. V.; Ribbe, P. H. *Am. Mineral.* **1971**, *56*, 782.

(17) Ichida, H.; Kobayashi, A.; Sasaki, Y. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1382.

Table II

$[H_2V_{10}O_{28}]^{4-}$	Σs	Evans' type	$[H_2V_{10}O_{28}]^{4-}$	Σs	Evans' type	$[H_2V_{10}O_{28}]^{4-}$	Σs	Evans' type	$[H_2V_{10}O_{28}]^{4-}$	Σs	Evans' type
V(1)	4.98	V(III)	O(6)	2.02	O(a)	O(11)	1.81	O(d)	O(16)	1.84	O(d)
V(2)	5.05	V(I)	O(7)	1.90	O(e)	O(12)	1.75	O(b)	O(17)	1.82	O(c)
V(3)	5.04	V(I)	O(8)	1.90	O(e)	O(13)	1.81	O(f)	O(18)	1.73	O(d)
V(4)	4.99	V(II)	O(9)	1.25	O(d)	O(14)	1.80	O(g)	O(19)	1.85	O(f)
V(5)	5.11	V(II)	O(10)	1.72	O(g)	O(15)	1.96	O(b)			

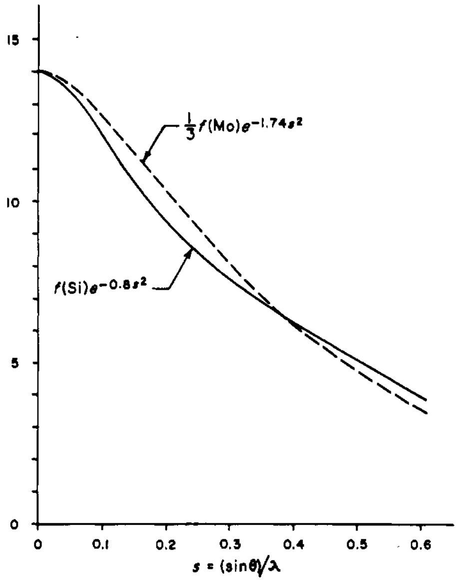

Figure 2. X-ray atomic scattering functions for $^1/_3$Mo with temperature factor as assumed by Yamase et al.[12] and for Si.

compound and stated that the crystals were obtained from a solution that had stood in a glass vessel for about 1 year and were accompanied by other crystalline phases that do contain dodecamolybdosilicate complexes. In light of these considerations, we believe that the Mo_{12}–Mo_{13} complex of Yamase et al. does not exist but is represented by an ordinary $SiMo_{12}$ Keggin molecule in a reduced state.

Dihydrogen Decavanadate,[18] $[H_2V_{10}O_{28}]^{4-}$

The decavanadate molecule ion has been studied in three crystal structures, as summarized by Evans.[1] Debaerdemaeker et al.[18] have recently published a new structure determination of the first acid, protonated, decavanadate species, which may be expected to illuminate the current controversy as to which oxygen sites would carry the H atoms.[19,20] They give no information about the preparation of the compound (presumably from an acid, aqueous environment), which is a 4-ethylpyridinium salt $(C_7H_9NH)_4[H_2V_{10}O_{28}]$, nor do they consider in any way the possible role of H atoms in the structure. With the well-refined structural data given, however, we are able to speculate on the latter question. The structure has the $[H_2V_{10}O_{28}]^{4-}$ complex located on a symmetry center at $^1/_2$, 0, $^1/_2$ in the crystal (space group $P2_1/n$, a = 19.473 Å, b = 9.938 Å, c = 11.965 Å, β = 92.26°, Z = 2, R = 0.08). The molecule is shown in Figure 3 with two of the four associated pyridinium groups. The pyridinium groups each form one N–H–O hydrogen bond with the molecule at O(12) and O(18) of lengths 2.62 and 2.71 Å, respectively, presumably supported by the pyridinium H atoms; all other N–O distances are greater than 3.5 Å. The two protons not associated with nitrogen must be located on some other O atoms in the molecule because there is no H_2O in the crystal.

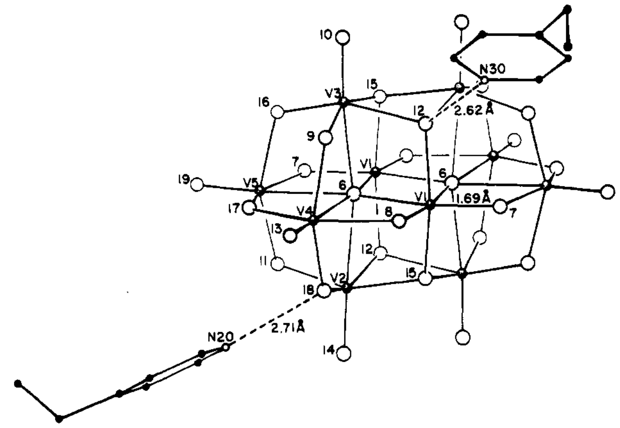

Figure 3. View of $[H_2V_{10}O_{28}]^{4-}$ after Debaerdemaeker et al.,[18] showing the two 4-ethylpyridinium molecules associated by hydrogen bonds. Recalculated bond lengths (in Å) are indicated for N–H–O hydrogen bonds and the V(1)–O(7) bond.

Debaerdemaeker et al. did not list interatomic distances in their report but indicate them on a figure similar to Figure 3 (they did not show the N–O distances, which we have calculated from their coordinates). Examination of their figure at once reveals an anomaly in the V(1)–O(7) bond given as 2.19 (1) Å, whereas in nonprotonated $[V_{10}O_{28}]^{6-}$ it is 1.69 Å, the same as V(1)–O(8).[1] This anomaly suggests that relaxation of the bonding to O(7) in the molecule allows O(7) to attach a H atom. However, recalculation of this bond length shows the figure to be in error: the actual length is 1.69 Å. All the other V–O bond lengths (confirmed by recalculation) are more or less normal, and so the question still remains: Where are the supernumerary protons? We have resorted to the use of empirical bond length/bond number calculations to try to find valence-deficient O atoms. For this purpose we have used the power function $s = (R/1.791)^{-5.1}$ developed by Brown,[21] which relates the V–O distance R and the bond number s. Using the model data and atom notation of Evans,[1] we find in the $[V_{10}O_{28}]^{6-}$ molecule that the valence sum at V(I) is 4.99, at V(II) 5.03, and at V(III) 4.88. For the central O atom O(a), the sum is 2.03. For the others, the sums are as follows: O(b) (triply linked), 1.82; O(c), O(d), and O(e) (doubly linked), 1.79, 1.72, and 1.84, respectively; O(f) and O(g) (terminal), 1.60 and 1.62. Klemperer and Shum[19] used these numbers to estimate the sequence of decreasing local negative charges: O(f) $\simeq$ O(g) < O(e) < O(c) < O(d) < O(b) < O(a) (their O_C = Evans' O(d) and O_D = Evans' O(c)). The apparent confusion on this point is moot because these empirical bond number sums are very approximate: in the range 1.60–1.84, all that can be said is that the charge is distributed more or less evenly over the whole molecule. Applying this method to the protonated molecule of Debaerdemaeker et al., we obtain a more striking result: see Table II. From these $\sum s$ values, we see that the central O(6) is properly saturated and that all the others except one are in the range 1.72–1.90. The exception is O(9), whose value of 1.25 is so low as to acquire

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(18) Debaerdemaeker, T.; Arrieta, J. M.; Amigo, J. M. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2465.

(19) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 3544.

(20) Howarth, O. W.; Jarrold, M. *J. Chem. Soc. Dalton Trans.* **1978**, 503.

(21) Brown, I. D. In "Structure and Bonding in Crystals"; O'Keefe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; Vol. II, pp 1–30.

special significance. This anomaly provides strong evidence that the extra proton is attached at O(9), a double linked O(d)-type atom.

Klemperer and Shum[19] studied the NMR spectra of ^{17}O in $[V_{10}O_{28}]^{6-}$ in solution at pH values in the range 4.5–6.0. By indirect reasoning based on peak shifts in the spectra, they concluded that the site of first acid protonation should be at the triply linked O(b). Howarth and Jarrold[20] studied the NMR spectra of ^{51}V over the pH range 2–9 and arrived at the conclusion (arguing against Klemperer and Shum but also by indirect reasoning) that first protonation should take place at the terminal O(g). Our treatment of the Debaerdemaeker et al. structure indicates a doubly linked O(d) site for first protonation. If O(d) is the site of the acid protons in the pyridinium salt crystal, it is quite possible that structure studies of other crystals containing the $[H_2V_{10}O_{28}]^{4-}$ species may reveal the protons to be located at other sites. We clearly are not in a position to predict these protonation sites with confidence. New structure analyses of protonated decavanadate compounds, preferably by neutron diffraction, are needed.

Registry No. $[PV_2Mo_{10}O_{40}]^{5-}$, 58071-93-5; $[PV_3Mo_9O_{40}]^{6-}$, 56188-77-3; $[PW_{12}O_{40}]^{3-}$, 12534-77-9; $[H_2V_{10}O_{28}]^{4-}$, 11117-82-1; $[SiMo_{12}O_{40}]^{4-}$, 50927-64-5.

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Chemical and Electrochemical Reduction of Pentacarbonyl(4-cyanopyridine) Complexes of Chromium(0), Molybdenum(0), and Tungsten(0)

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Group 6B metal carbonyl complexes having low-lying metal-to-ligand charge-transfer (MLCT) excited states are of current interest in inorganic photochemistry.[1] For a series of pentacarbonyl complexes of molybdenum and tungsten with various pyridines it has been shown that the lowest excited state is of MLCT character only if the pyridine is 4-substituted with a strongly electron-withdrawing substituent such as acyl or cyano, i.e. if there is an easily accessible π^* level of the heterocyclic ligand.[1-3]

The lowest unoccupied molecular orbital (LUMO) in such complexes can be populated through addition of an electron to yield the corresponding radical anion. For a ligand-centered LUMO, persistent π radicals may be expected, especially if the ligand itself already undergoes reversible one-electron reduction. During studies on the redox chemistry of the group 6B metal carbonyl complexes,[4,5] we have examined the reduction of chromium, molybdenum, and tungsten pentacarbonyl complexes of the heterocyclic ligand 4-cyanopyridine (**1**).

Results

Chemical and electrochemical reductions of the complexes $[\mathbf{1}\cdot M(CO)_5]$ in THF or DMF yield the paramagnetic species $[\mathbf{1}\cdot M(CO)_5]^{-\cdot}$ (Scheme I, route a). For M = W, the one-electron reduction is reversible, while in the case of Cr and Mo it has been found necessary to use additional metal hexacarbonyl in order to shift the dissociation equilibria in the closed reaction systems used to the radical complex side.

The radical complexes $[\mathbf{1}\cdot M(CO)_5]^{-\cdot}$ could also be generated in situ, either by reaction of the 4-cyanopyridine radical anion with hexacarbonylmetal in a replacement of one CO ligand (route b) or by a single electron-transfer reaction of decacarbonyldimetalate with the free ligand (route c). All these reaction pathways indicate the strong tendency for the formation of the radical complexes $[\mathbf{1}\cdot M(CO)_5]^{-\cdot}$.

The paramagnetic complexes have been characterized by high-resolution electron spin resonance (Figure 1); their formation was studied by cyclic voltammetry. Table I shows reduction potentials and ESR data of the complexes in comparison to the parameters of the free and of the N-methylated 4-cyanopyridine species.

Discussion

Several reaction pathways (Scheme I) lead to the formation of the radical anions of pentacarbonyl(4-cyanopyridine)-chromium, -molybdenum, and -tungsten. Reduction of the neutral complexes occurs at potentials considerably less negative than that of the reduction of the neutral ligand; almost half the effect of methyl quaternization is achieved by pentacarbonylmetal coordination (Table I). The ESR data show that the unpaired electron resides mainly in the ligand π system for all three radical anion complexes investigated; the coordination of $M(CO)_5$ to the radical ligand is, however, evident from the metal isotope splittings in the ESR spectra (Figure 1).

Perturbation effects of the coordinated metal pentacarbonyl groups on the ESR parameters are as expected;[4,5] this includes a marked increase of the pyridine ^{14}N coupling constant as well as a high g value for the tungsten complex (large spin–orbit coupling constant of tungsten). Particularly revealing is the behavior of the two hydrogen coupling constants $a_{H(2,6)}$ and $a_{H(3,5)}$, whose relation is reversed in the sequence of Table I. The chromium radical complex takes a special position in that it exhibits identical values for all the proton hyperfine coupling, thereby indicating that the acceptor function of the C–CN moiety is exactly matched by the effect of the N–$Cr(CO)_5$ group. For both the molybdenum and the tungsten derivatives, the electron-acceptor strength of the N-organometallic group seems to be greater than that of the cyano substituent at C(4). Nevertheless, despite the difference between the Mo and W species vs. the Cr radical complex the ESR and electrochemical results suggest a low-lying ligand-centered LUMO and low-energy MLCT transitions not only for molybdenum[3] and tungsten[1,2] but also for pentacarbonyl(pyridine)chromium complexes.

Preliminary studies in the 4-acylpyridine complex series[1-3] have shown that comparable reductions to persistent radicals take place.[6] Complete characterization of these radical complexes by ESR spectroscopy is impaired by their low symmetry due to the restricted C(4)–C_{acyl} rotation on the ESR time scale.[7]

In summation, the ESR results derived from one-electron reduction of these complexes prove the ligand character of their

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(1) Lees, A. J.; Adamson, A. W. *J. Am. Chem. Soc.* **1982**, *104*, 3804 and references cited therein.

(2) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105.

(3) Lees, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 2038.

(4) Kaim, W. *Inorg. Chim. Acta* **1981**, *53*, L151; *Chem. Ber.* **1982**, *115*, 910.

(5) Kaim, W.; Kasack, V. *Angew. Chem.* **1982**, *94*, 712; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 700.

(6) Kaim, W., to be submitted for publication.

(7) Rieger, P. H.; Fraenkel, G. K. *J. Chem. Phys.* **1962**, *37*, 2811.