glycinato complex, the other product is the Co(III) glyoxalato complex.

Sethuram et al.[11] consider the breaking of the N–H bond a fast step. Still, such an amino acid radical formation has been invoked in the Ag^+-catalyzed $S_2O_8^{2-}$ oxidation of α-amino acids.[12]

Registry No. I (R = H), 93922-97-5; I (R = CH_3), 93895-26-2; I (R = H, *N*-acetyl), 93895-27-3; I (R = H, *N*-benzoyl), 93895-28-4; I (R = CH_3, *N*-benzoyl), 93895-29-5; $(NH_3)_5Co^{III}L$ (L = glycine), 44982-38-9; $(NH_3)_5Co^{III}L$ (L = alanine), 34371-90-9; $(NH_3)_5Co^{III}L$ (L = *N*-acetylglycine), 80327-72-6; $(NH_3)_5Co^{III}L$ (L = *N*-benzoylglycine), 93895-30-8; $(NH_3)_5Co^{III}L$ (L = *N*-benzoylalanine), 93895-31-9; $(NH_3)_3Co(OH)_3Co(NH_3)_3^{3+}$, 45976-80-5; $(NH_4)_2Ce(NO_3)_6$, 10139-51-2; Ce, 7440-45-1; Co, 7440-48-4; glycine, 56-40-6; α-alanine, 56-41-7; *N*-acetylglycine, 543-24-8; *N*-benzoylglycine, 495-69-2; *N*-benzoylalanine, 2198-64-3.

Supplementary Material Available: A table of kinetic data for Ce(IV) oxidation of Co^{III} complexes of α-amino acids (1 page). Ordering information is given on any current masthead page.

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Structural Approach to the Behavior of ClO_4^- as a Ligand in Transition-Metal Complexes Using EXAFS, IR, and Raman Spectroscopy. 2.[1a] Crystal Structure of $M(ClO_4)_2$ (M = Co, Ni). A Novel Mode of Perchlorate Coordination

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Recently, new synthetic routes have allowed the preparation of a whole series of anhydrous metal perchlorates. Such compounds provide the unique opportunity of investigating the coordinating behavior of the perchlorate anion.[2,3] A number of X-ray crystal studies have already demonstrated weak bonding between the perchlorate anion and metal atoms,[4-9] but it was only recently that structural evidence of significantly strong metal perchlorate interactions has been obtained.[10,11] Interest in the anhydrous metal perchlorate family arises in part from their possible practical use as catalysts in cationic polymerization reactions. The perchlorates of magnesium, aluminum, cobalt(II), nickel(II), and copper(II) and the triflates (trifluoromethanesulfonates) of gallium and aluminum have recently been shown to be very active initiators of polymerization reactions in heterogeneous[12] and in homogeneous reaction systems.[13] Attempts to rationalize chemical reactivity in terms of atomic structure and intermolecular interactions require a detailed knowledge of the geometrical arrangement. However, the high reactivity of these complexes prevents the employment of the solvents usual in crystal growth, and solids are more often obtained in the form of microcrystalline powders. In the absence of single crystals suitable for complete radiocrystallographic investigation, structural information can be deduced by using spectroscopic techniques. Among these, extended X-ray absorption fine structure (EXAFS) spectroscopy is one of the most powerful, giving radial distances and information about the type and the number of scattering atoms.[14]

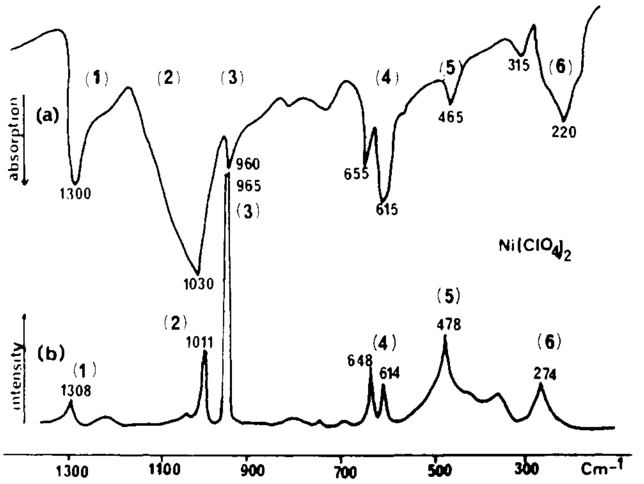

Figure 1. Vibrational spectra of $Ni(ClO_4)_2$: (a) infrared; (b) Raman. Peak assignments: (1) $\nu(Cl{=}O)$; (2) $\nu_{as}(ClO_3)_{coord}$; (3) $\nu_s(ClO_3)_{coord}$; (4) δ_{as}- and $\delta_s(ClO_3)_{coord}$; (5) $\delta(Cl{=}O)$; (6) $\nu(M–O)$.

A previous paper in this series described the study of copper perchlorate using EXAFS, infrared, and Raman spectroscopies.[15] The oxygen atoms of the perchlorate groups are strongly coordinated, with copper–oxygen distances of 1.96 Å, forming a square-planar arrangement around copper while two oxygen atoms at longer distances (2.67 Å) complete its coordination shell.

We present here an EXAFS study of cobalt and nickel perchlorates for which a regular octahedral MO_6 chromophore has been predicted,[16] thus making the analysis of EXAFS data much easier than for the copper analogue.

Experimental Section

A. Synthesis. The preparation of nickel and cobalt perchlorates used the general method described elsewhere for the synthesis of anhydrous metal perchlorates.[17] Anhydrous or hydrated metal chloride was allowed

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Table I. Results of the Fitting Procedure for $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ [d]

		$Co(ClO_4)_2$ (E_0 = 7723 eV)				$Ni(ClO_4)_2$ (E_0 = 8322 eV)			
atom	N^a	N^b	σ,[b] Å	R,[c] Å	ΔE_0,[c] eV	N^b	σ,[b] Å	R,[c] Å	ΔE_0,[c] eV
O(1)	6	7 (1)[d]	0.01 (9)	2.09 (1)	9 (1)	7 (1)	0.04 (1)	2.04 (1)	8 (3)
Cl	6	6 (1)	0.03 (2)	3.26 (2)	−6 (2)	5 (1)	0.03 (3)	3.24 (1)	−5 (3)
O(2)	6	7 (1)	0.05 (3)	3.43 (3)	10 (2)	6 (2)	0.01 (3)	3.42 (1)	8 (3)
O(3)	2	7 (2)	0.01 (10)	4.09 (5)	−1 (5)	2 (2)	0.01 (4)	4.06 (3)	−7 (3)
O(3), O(4)	12	10 (7)	0.06 (3)	4.20 (5)	−7 (6)	6 (5)	0.7 (7)	4.18 (5)	−7 (6)
M[c]	6	6 (2)	0.05 (2)	4.80 (2)	−3 (2)	6 (3)	0.06 (1)	4.80 (5)	3 (1)

[a] Theoretical values calculated for a $R\overline{3}$ $NiCl_2$ type structure. [b] Values of N and σ obtained by fitting the whole spectral range to 12.5 $Å^{-1}$, including all coordination shells with R and E_0 fixed. [c] Values obtained from a fit of each coordination shell treated separately after Fourier filtering. [d] In each case the standard deviation in parentheses refers to the last significant figure.

to react with a large excess of Cl_2O_6. (Methods of preparation, purification, and handling of Cl_2O_6 have already been reported.[18]) Removal of the excess of Cl_2O_6 under vacuum gave a solid product identified as $(ClO_2)[M(ClO_4)_3]$ (M = Co, Ni).

$M(ClO_4)_2$ was obtained by thermal degradation of the chloryl salt after being heated at 75 (cobalt) and 80 °C (nickel) for approximately 3 h. It has been reported that $Ni(ClO_4)_2$ can be obtained by dehydration of $Ni(ClO_4)_2 \cdot xH_2O$.[16,19] However, several attempts to obtain pure anhydrous nickel perchlorate using this route were unsuccessful.

The complexes were characterized by elemental analysis and X-ray powder diffraction. The powders are of poor crystalline quality; however, the similarity in their diffraction patterns suggested that they were probably of the same structural type. They can be indexed on the basis of a trigonal unit cell with a = 4.77 (2) Å, c = 21.85 (4) Å for $Ni(ClO_4)_2$ (which agrees with that previously reported[19]) and a = 4.83 (2) Å, c = 21.70 (4) Å for $Co(ClO_4)_2$.

B. Spectral Measurements. Nickel(II) and cobalt(II) perchlorates are highly hygroscopic, and special care was taken by handling the compounds in a glovebox under an atmosphere of dry nitrogen.

Infrared. Infrared spectra of the finely ground metal perchlorates were taken at room temperature by using silicon windows on a PE 180 spectrometer.

Raman. Raman spectra were recorded with a Dilor spectrometer and the data processed through a Tracor TN 1710 modular multichannel computer (Northern Instruments). The samples were sealed in Pyrex tubes and either were cooled to 180 K or were placed in a rotating cell at room temperature.

EXAFS. X-ray absorption spectra were recorded at 77 K with use of the synchrotron radiation source DCI at LURE, on the EXAFS 1 setup. The methods of handling the samples, treatment, and analysis of the data were as described in the first paper of this series.[15] The theoretically calculated amplitude and phase shifts of Teo et al. were used.[20,21]

Results and Discussion

The infrared and Raman spectra of $Ni(ClO_4)_2$ are presented in Figure 1. They are identical with those of the cobalt analogue. In the range 1400–400 cm^{-1}, the band frequencies and the pattern of absorption in the infrared spectrum agree with the published spectra of Rosolovskii et al.[16] Three major bands or lines are observed in the range of the stretching vibrations of the ClO_4 group and three in the range of the bending modes. This is consistent with a symmetry reduced from T_d for the unperturbated perchlorate ion to C_{3v} for the coordinated ClO_4. This situation could be realized with either monodentate or bridging tridentate coordination. However, the existence of monodentate perchlorate is unlikely since it requires twofold coordination for the metal. Furthermore the presence of a high-energy ClO stretching frequency at about 1300 cm^{-1} implies a large degree of double-bond character, which could be expected for a single non-metal-bonded oxygen.

Vibrational frequencies, and their assignments according to the above description, for the nickel compound are indicated in Figure 1. Bands at low frequencies in these spectra (220 cm^{-1}, IR; 274 cm^{-1}, Raman) are attributed to the metal–oxygen stretchings. They are found at slightly lower frequencies for the cobalt complex, which might indicate weaker M–O coordination.

Table II. Atomic Positions for $M(ClO_4)_2$ (M = Co, Ni)[a]

atom	x	y	z
M	0.0	0.0	0.0
Cl	0.0	0.0	0.254 (1)
O(1)	0.306 (1)	0.375 (1)	−0.057 (1)
O(3)	0.0	0.0	0.190 (1)

[a] Within the limits of the estimated standard deviations, atomic parameters are identical for Co and Ni complexes. The mean values are quoted.

The Fourier transform of EXAFS oscillations for $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ is shown in Figure 2[a,b]. These spectra are characterized by three main peaks. In a first attempt to model the structure, we considered these peaks as arising from M–O, M–Cl, and M–M backscattering (in increasing distance).

From a qualitive comparison of the Fourier-transformed EXAFS spectrum of cobalt or nickel perchlorates with that of the copper analogue (Figure 2c), differences in their structural types are apparent. In this last spectrum, the third peak, assigned to the metal–metal pair in the cobalt and nickel spectra, is absent and the ratio of the intensities of the second to the first peak is significantly increased. It is clear from Figure 2c that in the copper–copper compound, the M–M distance is shorter and backscattering of copper appears as a contribution to the composite second peak; this distance refines to 3.02 Å.[15]

When the theoretical phase shifts for oxygen, chlorine, and metal were introduced successively, the observed peak positions gave (a) M–O distances of 2.09 Å (cobalt) and 2.04 Å (nickel), which are identical with those found in several complexes of nickel and cobalt containing oxygenated ligands, (b) M–Cl distances of 3.26 Å, and (c) M–M distances of 4.80 Å. Subsequent filtering and nonlinear least-squares curve-fitting analysis confirmed these distances. However, while the agreement for the first and the third shells was acceptable, that for the second shell was poor. This is not surprising since the shape of the second peak in the Fourier transform clearly corresponds to a composite signal resulting from the overlap of several contributions.

At this stage of the structure determination, it was clear that the metal–chlorine and metal–metal distances and the number of atoms of each shell derived from EXAFS were fully consistent with a $CdCl_2$ or $NiCl_2$ type structure as previously suggested by Leborgne and Weigel for $Ni(ClO_4)_2$.[19] A model on the lines of a trigonal unit cell, type $NiCl_2$,[22] with a = 4.77 Å and c = 21.85 Å was therefore tested against the EXAFS data. It was immediately apparent that an undistorted $R\overline{3}m$ structure, with the ClO_4^- anion located on a site of $3m$ symmetry, was not an entirely adequate description. The M–O distance required in such a case would be about 1.8 Å, which is significantly shorter than the 2.04- and 2.09-Å distances obtained from EXAFS. The symmetry was thus modified in such a way as to allow rotation of the perchlorate group about the threefold axis. By this rotation, the space group symmetry is reduced to that of $R3$, given that the structure is not disordered. On this basis, all M–O and M–Cl distances up to 4.2

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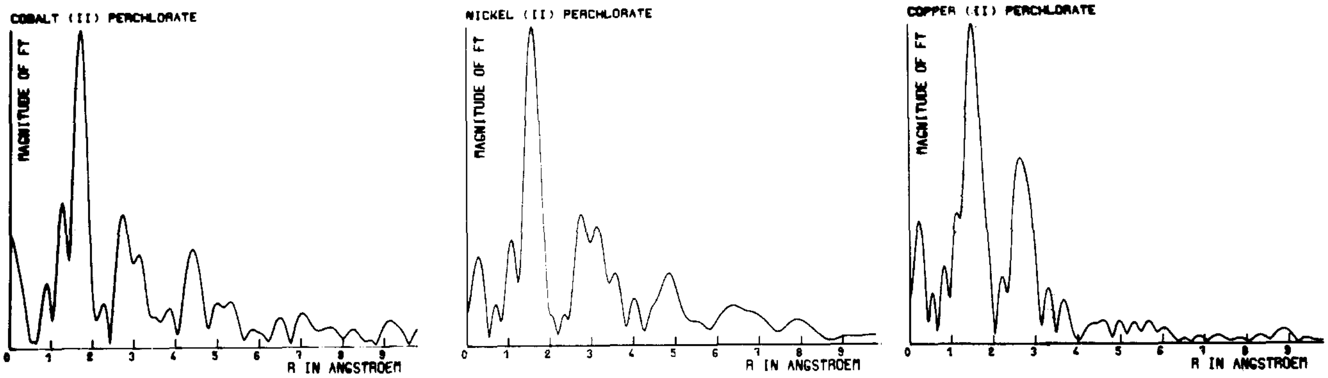

Figure 2. Fourier transform of the weighted EXAFS spectra in R-space ($k^3\chi(k)$ in arbitrary units vs. R in Å): (a) Co(ClO_4)$_2$; (b) Ni(ClO_4)$_2$; (c) Cu(ClO_4)$_2$.

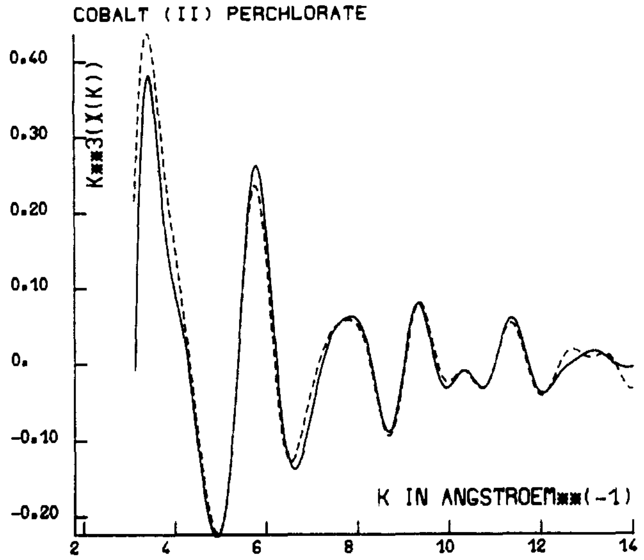

Figure 3. K-Space filtered spectra (solid line) with the corresponding calculated curves (dashed line) for Co(ClO_4)$_2$. The quality of the fit as estimated from the residual factor R ($R = \sum_k(\chi_{\text{exptl}} - \chi_{\text{calcd}})/\sum_k\chi_{\text{exptl}}^2$) is 3.5% ($R$ = 1.3% for Ni(ClO_4)$_2$).

Å could be calculated and we subsequently introduced in the refinements of the EXAFS data filtered between 1 and 4 Å. Good agreement was achieved (Figure 3), and the results are summarized in Table I.

A view of the structure down the threefold axis, with EXAFS-derived distances, is shown in Figure 4. It can be seen that the structure can be fully described by only five independent positional parameters, provided that the unit cell constants are known.

By use of the EXAFS-determined distances (Table I), it is therefore possible to derive a complete three-dimensional structure. Atomic coordinates are given in Table II. We are aware that for light atoms such as oxygen any attempts to refine parameters for shells as far away as 4 Å from the absorber could be regarded as being overoptimistic, but nevertheless, the procedure does succeed in giving a very realistic (if not very accurate) description of the coordinated perchlorate group with a Cl–O bond length of 1.44 (3) Å for the oxygen atoms bonded to the metal and 1.39 (5) Å for the "free" Cl–O bond length.

Another way of obtaining the geometry of the perchlorate group is to apply the concept of bond valence–bond strength, originally introduced by Pauling and recently refined by Brown and Shannon.[23,24] This approach entails the calculation of the bond valences between atoms M–O and O–Cl in the metal–oxygen–chlorine triplet from the empirical expression $V = (r/r_0)^{-N}$, where R_0 and N are universal fitted constants.

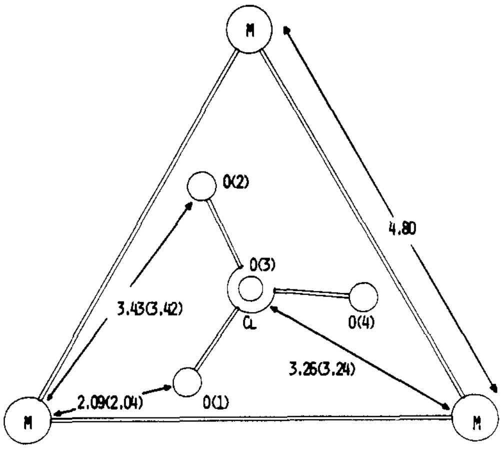

Figure 4. Proposed structure of M(ClO_4)$_2$ (M = Co, Ni), viewed down the threefold axis and showing notation and principal distances. Values in parentheses refer to Ni(ClO_4)$_2$.

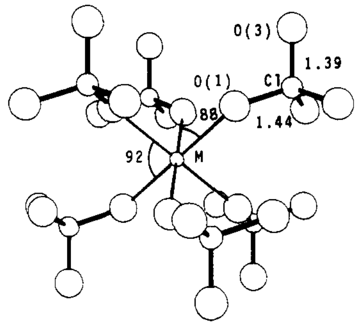

Figure 5. Environment of the metal atom in M(ClO_4)$_2$ (M = Co, Ni). Angles and distances are calculated from the data of Table II.

Assuming that the bond valences are such that their sum around each atom is equal to the formal ionic charge on that atom, the bond lengths $(Cl–O)_{coord}$ and $(Cl–O)_{free}$ may be calculated. The derived values $r(Cl–O)_{coord}$ = 1.45 Å and $r(Cl–O)_{free}$ = 1.39 Å agree with those obtained from the EXAFS data.

It is interesting to note that if this method is applied to Cu(ClO_4)$_2$, in which the ClO_4 group is bidentate and the M–O distance is significantly shorter (1.96 Å), the perchlorate group appears to be more distorted, with $r(Cl–O)_{coord}$ = 1.48 Å. Some recent structural investigations have shown strongly coordinated bidentate ClO_4 groups acting as a bridging ligand between two metal atoms, forming dimers[10,11] or infinite polymeric chains as in Cu(ClO_4)$_2$.[15] In these compounds, the presence of bidentate perchlorate is associated with a short metal–metal separation (3.0–3.2 Å) with a concomitant lengthening of the Cl–O bond (1.48 Å). The $\bar{3}$ symmetry of the environment about the metal atom is shown in Figure 5. The O–M–O angles are within ca. 2° of 90°, confirming the absence of any significant distortion from the regular octahedral geometry. The M–O–Cl angle is 136

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(1)°, which is in the range 125–160° generally observed for the M–O–X angle of coordinating tetrahedral XO_4^{n-} anions.[25]

Tridentate coordination of the ClO_4 group in nickel and cobalt perchlorates appears to be a direct consequence of the tendency of the metal atoms to retain a regular octahedral environment. Although examples of tridentate tetrahedral anions are frequently found, this type of coordination is the first to be structurally documented for the perchlorate anion.

The foregoing results are entirely consistent with infrared, Raman, and visible spectral data and magnetic measurements for $Co(ClO_4)_2$ and $Ni(ClO_4)_2$, which indicate a highly symmetrical structure and probable tridentate perchlorate.[16]

Acknowledgments. We gratefully acknowledge the help of the staff of the Laboratoire de l'Accélérateur Linéaire at Orsay, who operated the storage ring DCI. D.J.J. thanks the Royal Society of Great Britain and the French CNRS for the award of a European Exchange Fellowship. We thank Professor B. J. Hathaway (University College, Cork, Ireland) for his interest and useful comments about this work.

Registry No. $Co(ClO_4)_2$, 13455-31-7; $Ni(ClO_4)_2$, 13637-71-3.

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Reactions of Metal–Metal Multiple Bonds. 14. Synthesis and Characterization of *triangulo*-W_3 and -Mo_2W Oxo-Capped Alkoxide Clusters. Comproportionation of M–M Triple Bonds ($\sigma^2\pi^4$) and d^0 Metal–Oxo Groups: $M\equiv M + M\equiv O \rightarrow M_3(\mu_3\text{-}O)$

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The early transition elements niobium, molybdenum, and tungsten have recently been found to exhibit an extensive trinuclear chemistry with a variety of ligands.[1,2] Even the Mo(IV) aquo ions has been shown by a variety of spectroscopic techniques to contain the trinuclear unit $Mo_3O_4^{4+}$.[3-5] These complexes have *triangulo*-M_3 units capped by either one or two μ_3-X groups (X may be O, S, CR, etc.). The metal atoms are coordinated to six or seven ligand atoms, and the M_3 units have four to eight cluster electrons. Our interest in these compounds was heightened by the discovery of the simple comproportionation reaction shown in eq 1.[6,7] This provided a high-yield synthesis of a new subset of triangulo cluster compounds.

$$(RO)_3M\equiv Mo(OR)_3 + (RO)_4MoO \rightarrow Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_6 \quad (1)$$

$$R = i\text{-Pr and } CH_2\text{-}t\text{-Bu}$$

Reaction 1 has a parallel with the syntheses of dinuclear and trinuclear complexes employing metal–alkylidyne or –alkylidene fragments.[8] Reaction 1 also has a parallel with the reactions of alkynes with $Mo_2(OR)_6$ compounds, which give $Mo_2(\mu\text{-}C_2R_2)$ compounds containing the pseudotetrahedral M_2C_2 core.[9] One might well wonder whether or not one could extend comproportionation μ_3-X of type 1 to include other metal atoms and other ligands; e.g. can one replace Mo by W, O by S, NR and OR by SR, etc. We describe here our initial findings, which were prompted by these considerations.

Results and Discussion

Synthesis. $W_3O(O\text{-}i\text{-}Pr)_{10}$. Since $W_2(O\text{-}i\text{-}Pr)_6$ is not isolable in an unligated form,[10] the crystalline compound $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$[11] was used along with $WO(O\text{-}i\text{-}Pr)_4$[12] for the comproportionation reaction. Mixing the two compounds in hexane followed by heating gave a royal blue solution from which dark blue crystals of $W_3O(O\text{-}i\text{-}Pr)_{10}$ were obtained.

$Mo_2WO(O\text{-}i\text{-}Pr)_{10}$. The addition of $WO(O\text{-}i\text{-}Pr)_4$ to a hexane solution of $Mo_2(O\text{-}i\text{-}Pr)_6$ followed by heating results in an orange to green color change, and by crystallization the mixed-metal triangulo compound $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$ can be isolated as green crystals.

$MoW_2O(O\text{-}i\text{-}Pr)_{10}$. In an attempt to prepare the related MoW_2-containing compound, $MoO(O\text{-}i\text{-}Pr)_4$ and $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ were allowed to react in hexane. An immediate reaction occurred as evidenced by a color change to green. However, the reaction was more complicated than had been hoped. Attempts to crystallize the trinuclear compound failed. First fine white needles of the relatively insoluble compound $WO(O\text{-}i\text{-}Pr)_4$ were obtained. Then, from crystallization of the filtrate, blue-green crystals were obtained. The ^1H NMR spectrum of the latter indicated the presence of $W_3O(O\text{-}i\text{-}Pr)_{10}$ and other species, possibly the desired $MoW_2O(O\text{-}i\text{-}Pr)_{10}$.

Our interpretation of this is that the oxo-group-transfer reaction in eq 2 is favored and the further reaction of $WO(O\text{-}i\text{-}Pr)_4$ with $W_2(O\text{-}i\text{-}Pr)_6$ and $MoW(O\text{-}i\text{-}Pr)_6$ yields $W_3O(O\text{-}i\text{-}Pr)_{10}$ and $MoW_2O(O\text{-}i\text{-}Pr)_{10}$, respectively.

$$MoO(O\text{-}i\text{-}Pr)_4 + W_2(O\text{-}i\text{-}Pr)_6 \rightarrow MoW(O\text{-}i\text{-}Pr)_6 + WO(O\text{-}i\text{-}Pr)_4 \quad (2)$$

This suggestion finds support in the observations of Hoskins,[13] who found that, while the homonuclear *tert*-butoxides failed to react ($M_2(O\text{-}t\text{-}Bu)_6 + (t\text{-}BuO)_4MO$, M = Mo and W), the addition of $(t\text{-}BuO)_4MoO$ to $W_2(O\text{-}t\text{-}Bu)_6$ in hydrocarbon solvents yielded an immediate color change from yellow-orange to green but with time the yellow-orange color returned and by crystallization only a mixture of homonuclear, Mo_2 and W_2, and heteronuclear MoW hexa-*tert*-butoxides were obtained. The formation of $MoW(O\text{-}t\text{-}Bu)_6$ in this reaction can reliably be established by NMR spectroscopy and by mass spectrometry, but it cannot be separated from the Mo_2- or W_2-containing compounds by crystallization. Thus we believe that in the present instance $MoO(O\text{-}i\text{-}Pr)_4$ and $W_2(O\text{-}i\text{-}Pr)_6$ react to give $MoW_2O(O\text{-}i\text{-}Pr)_{10}$ but that this is unstable with respect to dissociation to $MoW(O\text{-}i\text{-}Pr)_6$ and $WO(O\text{-}i\text{-}Pr)_4$. The latter then react to give $W_3O(O\text{-}i\text{-}Pr)_{10}$, $MoW_2O(O\text{-}i\text{-}Pr)_{10}$, $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$, and $Mo_2(O\text{-}i\text{-}Pr)_6$.

Attempted Preparations of $MM'_2(O\text{-}i\text{-}Pr)_{11}$ Compounds Where M = Nb, Ta and M′ = Mo, W. Since it is possible for RO ligands to cap the triangle of metal atoms once, why not twice? In attempts to prepare compounds of formula $MM'_2(\mu_3\text{-}O\text{-}i\text{-}Pr)_2(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$, hydrocarbon solutions of $M(O\text{-}i\text{-}Pr)_5$ (1 equiv), where M = Nb and Ta, and $Mo_2(O\text{-}i\text{-}Pr)_6$ or $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ were mixed and heated. No evidence for a com-

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