

In order to see how the magnetic results conform to the two possible bonding schemes proposed for the complexes, the magnetic moments were calculated as a function of temperature by using the computer program CAMMAG. The only parameter required in this procedure in addition to the metal-ligand bonding parameters, interelectron repulsion parameters, and spin-orbit coupling constants used to estimate the energy levels in the complexes is an orbital reduction parameter k .¹⁰ As may be seen from Figure 2, it was found that excellent agreement with the experimentally observed magnetic moments was obtained over the complete temperature range for both complexes using values of $k = 0.9$ and 0.95 for the Ni(II) and Co(II) complexes, respectively, with the metal-ligand bonding parameters appropriate to assignment A of the d-orbital energies (Figure 1). The relatively high values of k , which suggest that the bonding to the central metal ions is quite ionic, are consistent with the fact that the Co(II) and Ni(II) ions are surrounded by four oxygen ligand atoms and two distant Pt(II) ions.

The scheme A ascribes the steep decrease in μ at low temperature of the Ni(II) complex to a zero-field splitting of the ground state of 7 cm^{-1} caused by spin-orbit coupling to excited electronic states split by the substantial difference between the "ligand field" of the axial Pt(II) ions ($e_\sigma = 1247 \text{ cm}^{-1}$) and the in-plane oxygen ligands ($e_\sigma = 5265 \text{ cm}^{-1}$). In contrast, the gradual decrease in μ observed below $\sim 120 \text{ K}$ for the Co(II) complex is derived in this scheme from the splitting of the ground state by an amount comparable to normal thermal energies (Figure 1), this being caused by a combination of the tetragonal component of the ligand field and spin-orbit coupling.

For both complexes the magnetic moments calculated by using assignment B of the d-orbital energies are in very poor agreement with the observed values (Figure 2). In particular, for the nickel(II) complex, this scheme predicts a much larger value of the magnetic moment at room temperature than is observed experimentally, this being related to the very large tetragonal component of the ligand field implied by the bonding parameter of the axial Pt(II) "ligands" ($e_\sigma = -2342 \text{ cm}^{-1}$). This causes the E component of the ${}^3T_{2g}$ state of the parent octahedral complex to drop so substantially that it approaches the ground state in energy (Figure 1), producing a magnetic moment similar to that of a complex with an orbital triplet ground state.⁹ Moreover, the very large zero-field splitting of the ground state predicted by scheme B (40 cm^{-1}) would suggest that on cooling the magnetic moment of the Ni(II) complex should start to decrease at a much higher temperature than is observed experimentally (Figure 2).

It is thus apparent that the magnetic measurements strongly support d-orbital energy sequences for the central metal ions in the trimers which imply that the terminal Pt(II) ions effectively function as normal ligands, producing weak antibonding interactions with the d orbitals that are consistent with the rather long metal-metal distances observed in the trimers ($\sim 270 \text{ pm}$).^{3,11} The excellent agreement between the calculated magnetic moments and those observed experimentally, obtained without altering the bonding and interelectron repulsion parameters derived from the electronic spectra, illustrates both the value of carrying out magnetic measurements on compounds of this kind and the power of ligand field calculations performed with computer programs such as CAMMAG in interpreting the spectral and magnetic properties of transition-metal complexes.

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Contribution from the Pittsburgh Energy Technology Center,
Pittsburgh, Pennsylvania 15236

Metals for Which Crystalline Anhydrous Sulfates Are Not Known

Sidney S. Pollack

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In the study of potential sorbents for the removal of SO₂ from flue gas, the question arose as to the formation of "molybdenum sulfate". After a short search, it became evident that no "molybdenum sulfate" had been reported in the literature. Further search identified other metals for which no data on simple anhydrous sulfates existed. All the alkali and alkaline earth metals, the first transition series, and metals from groups III-VI (groups 13-16)¹³ except Ge form crystalline simple anhydrous sulfates. However, in the second and third transition series, all metals except Nb, Mo, Tc, Ru, Pd, W, Re, Os, Ir, Pt, and Au form simple sulfates. The positions of these elements in the periodic table relative to some of the metals in the first transition series are shown below to the left. On the right are shown the metals in the second and third transition series for which simple anhydrous phosphates are not known.

Sulfates											Phosphates						
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn									
		Nb	Mo	Tc	Ru		Pd					To	Ru	Rh	Pd		
		Ta	W	Re	Os	Ir	Pt	Au				W	Re	Os	Ir	Pt	Au

The statement that anhydrous sulfates are not known is based on the absence of simple anhydrous sulfates from the *Powder Diffraction File*¹ and from *Chemical Abstracts*. Molybdenum and niobium do not form simple anhydrous sulfates but do crystallize as the binary metal sulfate hydrates K₃Mo₂(SO₄)₄·3.5H₂O,² K₄Mo₂(SO₄)₄·2H₂O,³ and K₄(H₃O₂)[Nb₃O₂(SO₄)₆·(H₂O)₃]·5H₂O.⁴ Size does not appear to be a critical factor, since there is an overlap in atomic radii between the elements that do and do not form anhydrous sulfates.⁵

Although PdSO₄·2H₂O and Pt(SO₄)₂·4H₂O are listed in the *Handbook of Chemistry and Physics*,⁶ no structural information is available for these compounds. X-ray powder diffraction data have been reported for Ta₂O₃(SO₄)₂·0.5H₂O,⁷ but no structure has been described. The *Powder Diffraction File* lists even fewer simple anhydrous nitrates than sulfates and phosphates.¹ Addison and Logan summarized much information about anhydrous nitrates and showed a chart of the periodic table indicating the metals that form anhydrous metal nitrates.⁸ They explained the absence of Ti, Nb, and Ta anhydrous nitrates on the basis that these metals would be expected to be present as covalent nitrates in their highest oxidation state. This would mean an unfavorable coordination number of five or a higher coordination number that would not be acceptable on steric grounds. They offered no explanation for the absence of the other simple anhydrous metal sulfates except osmium, which they indicated had not received a great deal of study. As of this work, no additional anhydrous nitrates have been reported.

Most of the metals that form anhydrous sulfates have an oxidation state of +2 or +3 except for the alkali metals, which have a +1 oxidation state. Titanium, which can have +1, +2, +3, and

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+4 oxidation states, only forms an anhydrous sulfate with a +3 state, while Hf and Zr both form anhydrous sulfates with a +4 state. Except for Ta (+5), Tc (+7), and Au (+1 or +3), all of the metals for which anhydrous sulfates are not known commonly are present as +4 in other compounds. In the structure $Zr(SO_4)_2$, each Zr atom is in sevenfold coordination with bonds to one oxygen of each of seven sulfate tetrahedra.⁹ Each Mo in both $K_4Mo_2(SO_4)_4 \cdot 2H_2O^3$ and $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O^2$ is bonded to oxygen atoms of each of five sulfate tetrahedra and to one Mo atom, resulting in a $Mo_2(SO_4)_4^{4-}$ ion in the former structure and a $Mo_2(SO_4)_4^{3-}$ ion in the latter. Thus, the coordination of the Mo and Zr in these compounds is very different. In the structure of $K_4(H_3O_2)[Nb_3O_2(SO_4)_6(H_2O)_3] \cdot 5H_2O$, the Nb occurs as $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$.⁴ The Nb atoms form a triangular cluster, where each Nb is bonded to two other Nb atoms rather than to just one metal atom as occurs in the Mo structure mentioned above. Like the Mo in the above two Mo-containing compounds, the Re in $Na_2Re_2(SO_4)_4 \cdot 8H_2O$ is coordinated by five oxygens and another Re atom.¹⁰

In all the known simple anhydrous sulfates, the metals are bonded only to oxygens from the sulfate groups, and no metal-to-metal bonding is present. For Mo, Re, and Nb, only complex binary sulfate hydrates in which the Mo, Re, and Nb are bonded to other Mo, Re, and Nb atoms as well as to oxygen atoms have been described. Cotton suggested that in compounds other than carbonyls, Nb, Mo, Tc, Ta, W, and Re formed metal-metal bonds much easier than did the other metals in the second and third transition series.¹¹ If his idea is correct, then sulfates of these metals may not be known because earlier attempts at syntheses may have used starting materials such as MoO_2 , which contains a metal-metal bond¹² or the bond may have formed during synthesis and prevented anhydrous sulfate formation. Use of the proper starting materials and avoidance of metal-metal bond formation during synthesis may be necessary for the crystallization of these anhydrous sulfates that have never been crystallized.

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Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

Observation of a Novel ^{31}P NMR Cis-Influence Series: Implications for the Relative Basicity of PPh_3 and PMe_3 in Tungsten Carbonyl Complexes

Robert V. Honeychuck and William H. Hersh*

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The correlation of ligand donor strength with trends in spectroscopic data has been sought repeatedly.¹⁻⁶ The attraction of

Table I. ^{31}P NMR Data for 1

entry	L	PMe_3		L		
		δ^a	$^1J(P-W)^b$	δ	$^1J(P-W)$	$J(P-P)$
1	SbF_6^-	-16.25 ^c	282.9			
2	PF_6^-	-16.64 ^d	283.2	-139.30 ^e	0	0
3	BF_4^-	-17.46 ^f	282.0			
4	acetone	-20.40	275.5			
5	$C_6H_9CHO^g$	-20.42	277.1			
6	acrolein	-20.45	276.6			
7	Me_2SO_2	-21.07	275.9			
8	camphor	-21.07	274.7			
9	Me_2NCHO	-21.10	276.5			
10	$PF_5O_2^-$	-21.48	274.4	-17.35 ^h	0	4.7
11	EtOH	-21.49	272.8			
12	CD_3OD	-21.61	272.8			
13	D_2O	-21.85	273.6			
14	THF	-21.92	274.4			
15	MeCN	-27.03	263.8			
16	Et_3N	-28.34	264.9			
17	Ph_3P	-35.96	252.4	9.29	178.2	23.2
18	$MePh_2P$	-36.55	251.0	-14.56	172.3	23.6
19	Me_2PhP	-36.92	251.5	-31.26	165.4	23.6
20	Me_3P	-37.45	250.1	-42.57	163.4	24.6
21	Cl^-	-28.34	263.8			
22	Br^-	-34.43	263.7			
23	I^-	-44.83	261.9			
24	CO^i	-33.23	244.1			
25	$(MeO)_3P$	-34.76	247.6	109.73	286.0	38.4
26	Cy_3P^j	-38.92	252.8	25.64	219.1	21.9

^a ppm; negative values upfield of H_3PO_4 . ^b Hz. ^c Septet, $J_{PF} = 39.8$ Hz. ^d Broad singlet. ^e Septet, $J_{PF} = 731.7$ Hz. ^f Quintet, $J_{PF} = 39.7$ Hz. ^g Diels-Alder adduct of butadiene and acrolein. ^h Triplet, $J_{PF} = 966.2$ Hz. ⁱ Structure in question; see text. ^j Cy = cyclohexyl.

such an approach is that widely divergent ligand types can be examined fairly readily and more importantly be compared to each other. Conventionally, infrared¹ and NMR^{2,3} data have been used and are directly applicable if one assumes a direct correlation of ligand donor strength with ligand trans influence.^{4,5} More recently, spectra that probe electronic energy levels have also been used to compare ligand donor strength,^{4,6} in a study of $PtCl_3L^-$ complexes,⁶ PEt_3 was found to be a better donor than PPh_3 , while in a study of tungsten carbonyl phosphine complexes, the provocative conclusion was reached that PPh_3 is a better donor than PMe_3 ,⁴ a direct challenge to the common wisdom.⁷ In fact, the infrared and NMR data brought to bear on the question of phosphine basicity toward tungsten carbonyl fragments are undeniably equivocal,^{3,4} even though broader trends are often in accord with expectation. For instance, Schenk has reported two trans-influence series based on $^1J(^{183}W-X)$ ($X = ^{31}P, ^{13}C$) in $trans-LW(CO)_4X$ ($X = PR_3, CO$).³ When strictly applied to the narrow region of $L = P$ -donor ligands, however, his results suggest the basicity order $P(OPh)_3 > P(i-Pr)_3 > PPh_3$ based on $trans-LW(CO)_4(P-i-Pr_3)$ but $P(OPh)_3 > PPh_3 > PMe_3$ based on $LW(CO)_5$. The differences in the coupling constants are not large however—Schenk grouped the three ligands together—and of course, the common wisdom would hold that $P(OPh)_3$ is also misplaced in these series.⁷ The question we wish to address here, then, is whether a simple NMR-derived ligand series can be found that is reliable both for a broad series of ligands and for the narrower range of phosphines. We report here a novel ^{31}P NMR cis-influence series based on both chemical shifts and phosphorus-metal coupling constants

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