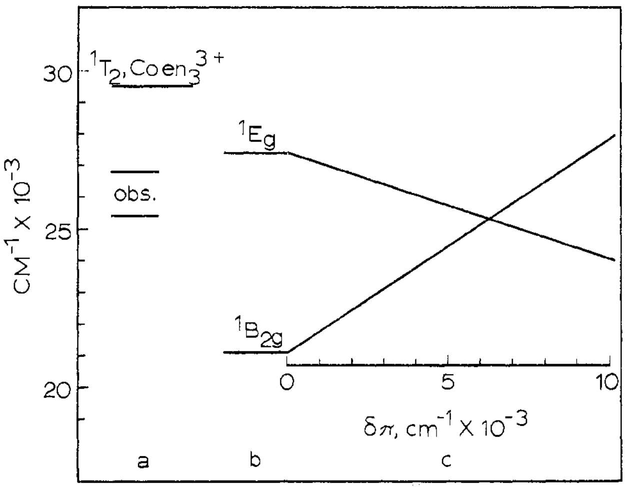

Figure 2.—(a) The observed wavenumber of the $^1T_2$ absorption in $Co(en)_3^{3+}$ and the wavenumbers of the high-energy bands from the polarized crystal spectra of *trans*-$[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$. (b) The predicted wavenumbers of the $^1E_g{}^b$ and $^1B_{2g}$ absorptions with $\delta\Delta = -12{,}600$ cm^{-1} and $\delta\pi = 0$. (c) The predicted wavenumbers of these absorptions as a function of $\delta\pi$.

bromide, the unobserved and unresolved $^1T_2$ band should occur in solution at 4000 to 5000 cm^{-1} lower than the corresponding 29,500 cm^{-1} absorption in $Co(en)_3^{3+}$. From the crystal spectra the bands in question occur at 4100 and 2700 cm^{-1} lower than the absorption in $Co(en)_3^{3+}$, with $\delta\Delta$ evaluated as $-12{,}600$ cm^{-1}. It is difficult to believe that this agreement is fortuitous and altogether reasonable to assume that these two bands arise from the splitting of the $^1T_2$ state.

The ordering of the components of this state presents a more serious problem. With small π bonding by bromide ion the $^1E_g{}^b$ state should lie higher than the $^1B_{2g}$ state, but with increasing π bonding the energy separation decreases until at $\delta\pi = -{}^1/_2\delta\Delta$ (6300 cm^{-1}) these states cross. In Figure 2 it can be seen that the best fit of the observed spectrum is obtained with $\delta\pi > 6300$ cm^{-1}. A better fit can be had by assuming both bands are allowed in either polarization,[8] thereby increasing the splitting somewhat. Without resorting to Gaussian analysis, it is not unreasonable to choose $\delta\pi \approx 9000$ cm^{-1}.[9] The splittings of the one-electron energy levels are then as follows[10]

$$E(b_{1g}{}^*) - E(b_{2g}) = \Delta^{en} \qquad = 25{,}300 \text{ cm}^{-1}$$

$$E(a_{1g}{}^*) - E(b_{2g}) = \Delta^{en} + {}^2/_3\,\delta\Delta + {}^2/_3\,\delta\pi \approx 22{,}900 \text{ cm}^{-1}$$

$$E(e_g{}^*) - E(b_{2g}) = {}^1/_2\,\delta\pi \qquad \approx 4500 \text{ cm}^{-1}$$

The energy separation between the $e_g{}^*$ and b_{2g} orbitals is perhaps unexpectedly large and there are no means in hand to ensure the reliability of this result. A smaller choice of $\delta\pi$, although resulting in a poorer fit of the spectra, would have reduced this separation. It is hoped, however, that investigations of the circular dichroism of the complete series of *trans*-dihalobis(*cis*-cyclohexanediamine)cobalt(III) ions, which is currently in progress at the University of Illinois, will eventually lead to an unambiguous assignment.

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[8] Such an assumption is not unwarranted. If, as in ref 7, the effective symmetry was taken as D_{4h}, vibronic selection rules indicate that transitions to the $^1E_g{}^b$ and $^1B_{2g}$ states are allowed in either polarization. Therefore in any lower symmetry retaining the center of inversion, transitions to the states which correlate to those in D_{4h} symmetry will always find allowance in either polarization providing the axis of quantization remains coincident with the cobalt–halide radius vector.

[9] Configurational interaction between the ^1E_g states has been neglected in arriving at this result. For *trans*-CoA_4X_2, the requisite off-diagonal matrix element is $\sqrt{3}/6(\delta\Delta + \delta\pi)$. Using the values of $\delta\Delta$ and $\delta\pi$ derived in the text, this matrix element is only equal to 1040 cm^{-1}, a negligible amount. It should be noted that an analogous treatment of CoA_5X indicates that the contributions of $\delta\Delta$ and $\delta\pi$ should be multiplied by one-half.

[10] See H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958), and reformulation in ref 2.

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Stereochemistry and P=O Bond Order in Trialkyl Phosphate Extractants

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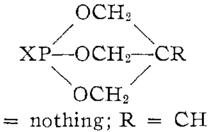
Our recent investigations of the ligand properties of polycyclic phosphites such as I with first-row transition metal ions,[1] transition metal carbonyls,[2] and boron-containing Lewis acids[3] revealed that constraint of the alkoxy moieties on the phosphorus allowed formation of strong-field complexes, strongly π-bonded complexes, and stable adducts, respectively. These results prompted us to investigate the rare earth extractant properties of the bicyclic phosphate 1-oxo-4-pentyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane(IV), which is similar in structure to tri-*n*-butyl phosphate (TBP) except for the drastically reduced steric requirement. Compound IV was more desirable than II for this investigation, since it is far less soluble in aqueous acid than II. The reversed phase partition chromatographic technique described by Banks and O'Laughlin[4] was employed to show that IV does not function as an extractant for trivalent lanthanum, neodymium, samarium, gadolinium, and ytterbium ions under the variety of conditions herein described.



I, X = nothing; R = CH_3
II, X = oxygen; R = CH_3
III, X = nothing; R = $(CH_2)_4CH_3$
IV, X = oxygen; R = $(CH_2)_4CH_3$

Experimental Section

Preparation of IV.—The synthesis of $CH_3(CH_2)_4C(CH_2OH)_3$ was carried out in a manner similar to that described by Dermer

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[1] T. J. Huttemann, Jr., B. M. Foxman, C. R. Sperati, and J. G. Verkade, *Inorg. Chem.*, **4**, 950 (1965).

[2] J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *ibid.*, **4**, 228 (1965).

[3] J. G. Verkade, R. W. King, and C. W. Heitsch, *ibid.*, **3**, 884 (1964).

[4] C. V. Banks and J. W. O'Laughlin, *Anal. Chem.*, **36**, 1222 (1964).

and Solomon[5] for similar alcohols. In this case a mixture of 112 g (2.00 moles) of calcium oxide, 973 g of formalin (12.0 moles of formaldehyde), 80 ml of 2% aqueous aerosol OT solution, 3 l. of water, and 536 ml (4.00 moles) of heptanaldehyde was heated with stirring to 60°. The mixture was allowed to cool to room temperature, neutralized with 20% sulfuric acid, and filtered. The organic layer of the filtrate was separated, washed with water, and distilled at 193° (9 mm) to give a light yellow syrup which crystallized on standing. The product was recrystallized from benzene to give 67 g (9.5% yield) of $CH_3(CH_2)_4C(CH_2OH)_3$, mp 65–68°.

Anal. Calcd for $C_9H_{20}O_3$: C, 61.4; H, 11.4. Found: C, 62.2; H, 11.9.

The intermediate bicyclic phosphite III was prepared in a manner similar to that described by Wadsworth and Emmons[6] for analogous compounds. A mixture of 10 g (0.057 mole) of $CH_3(CH_2)_4C(CH_2OH)_3$ and 7.1 g (0.057 mole) of trimethyl phosphite was heated to 130° during which time 6 ml of methanol distilled off. The remaining methanol and unreacted trimethyl phosphite were removed by heating under vacuum at 100° for 0.5 hr. The residue solidified on standing and was recrystallized from *n*-pentane to yield 8.4 g (72% yield) of colorless product which melted from 45 to 48° after subliming under vacuum at 38°.

Anal. Calcd for $C_9H_{17}O_3P$: C, 52.94; H, 8.33. Found: C, 51.91; H, 8.41.

Compound IV was prepared following a procedure previously described[7] in which 3.0 g (0.026 mole) of 30% hydrogen peroxide was added dropwise with stirring to a solution of 5.4 g (0.026 mole) of III in 10 ml of absolute ethanol. After the exothermic reaction ceased, the mixture was cooled to ice temperature. The yield of colorless crystalline product melting from 134 to 137° thus obtained was 3.7 g (64%).

Anal. Calcd for $C_9H_{17}O_4P$: C, 49.09; H, 7.72. Found: C, 49.83; H, 7.93.

The structural assignments of IV and the parent phosphite were substantiated by their proton nmr spectra. Using a Varian HR-60 spectrometer, spectra were obtained in deuteriochloroform solutions with tetramethylsilane as an internal standard. For both compounds the pentyl group chemical shift ranged from 0.62 to 1.66 ppm with prominent peaks at 0.87 and 1.23 ppm. A doublet due to spin–spin coupling from the phosphorus nucleus ($J_{POCH} = 2.0$ cps) was observed at 3.90 ppm in the case of the parent phosphite whereas in the spectrum of IV a similar doublet ($J_{POCH} = 6.6$ cps) appeared at 4.49 ppm. In both cases the expected ratio of intensities of the methylene and pentyl group proton peaks was observed.

Stock solutions of 0.1 *M* lanthanum, neodymium, samarium, and gadolinium nitrate in 0.5 *M* nitric acid were prepared from the trivalent metal nitrates. A weighed amount of ytterbium(III) oxide was converted to the nitrate and perchlorate salts by a standard method[8] and made 0.1 *M* in the corresponding acid. These solutions were spotted by means of a finely tipped eye dropper on the center of Whatman 41 filter paper disks. The disks were previously impregnated with 0.20 or 0.71 *M* chloroform solutions of IV or a 0.75 *M* solution of TBP in carbon tetrachloride. After slowly drawing the disks through the impregnating solutions, they were allowed to dry on flat aluminum foil to ensure uniform distribution of the stationary phase. The amount of extractant on the paper was obtained by weighing before and after impregnation. The two concentrations of IV and that of TBP were thus 3.3×10^{-6}, 1.31×10^{-5}, and 1.19×10^{-5} mole/cm², respectively. Chromatograms were developed in Petri dishes using 0.5, 3.0, 6.0, and 9.0 *M* nitric acid and 0.05, 0.50, and 1.0 *M* perchloric acid. Development time was usually several hours for papers treated with TBP and about 0.5 hr with those treated with IV. Chromatograms were developed to within 2 or 3 cm of the edge and the metal ion zones were detected by drying the paper and treating with gaseous ammonia to neutralize excess acid, followed by spraying with a 0.5% solution of 8-hydroxyquinoline in 60% by volume ethanol in water.

TABLE I

P=O STRETCHING FREQUENCIES AND DIPOLE MOMENTS

	P=O stretch, cm^{-1}	Dipole moment, D	$\Delta\mu$
$(CH_3O)_3P$		1.83[a]	
			1.19
$(CH_3O)_3P{=}O$	1274	3.02[a]	
$(CH_3(CH_2)_3O)_3P$		1.92[a]	
			1.17
$(CH_3(CH_2)_3O)_3P{=}O$ (TBP)	1260	3.09[a]	
I		4.15[b]	
			2.95
II	1325	7.10[b]	
IV	1325		

[a] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963. [b] T. L. Brown, J. G. Verkade, and T. S. Piper, *J. Phys. Chem.*, **65**, 2051 (1961).

It was found that IV was increasingly soluble in concentrations of nitric acid greater than 6.0 *M*. To ensure that IV was not moving significantly with the solvent front in 6.0 *M* nitric acid, a paper was developed in this acid. After drying, it was cut into four concentric rings of equal width, each ring was extracted with boiling chloroform for 2 hr, and the extracts were evaporated to 1 ml. A comparison of the intensities of characteristic bands of IV in a similarly treated ring of the same size from an undeveloped paper showed that no movement of IV with the solvent front took place. No appreciable solubility of IV in the other developing solvents was found.

Results and Discussion

Retention values (R_r) for TBP for the lanthanide nitrates in 0.5, 3.0, 6.0, and 12 *M* nitric acid were 1.0 for lanthanum and neodymium, while for the remaining metals they were: samarium, 1.0, 1.0, 0.93, 0.84; gadolinium, 1.0, 1.0, 0.95, 0.77; and ytterbium, 1.0, 1.0, 0.89, 0.48. In all cases where the lower concentration of IV was used, however, R_r values were consistently 1.0 even when the higher concentration of IV was used for ytterbium in 6.0 *M* nitric acid. Retention values were also obtained for ytterbium perchlorate solutions in 0.00, 0.05, 0.50, and 1.0 *M* perchloric acid. With TBP these values were 0.89, 0.92, 0.92, and 0.95, respectively, while with the lower concentration of IV values of 1.0 were always obtained. Using the higher concentration of IV in 0.00 or 0.05 *M* perchloric acid also gave $R_r = 1.0$.

There is a surprising lack of extraction properties for IV compared to the more bulky TBP. Moreover, the substantially higher dipole moments shown in Table I associated with bicyclic phosphates compared to analogous open-chain systems might be expected to lead to a stronger cation–dipole interaction and hence produce R_r values of less than unity.

The lack of extraction ability of IV can be explained in terms of the extraordinary degree of π bonding between the phosphorus and the phosphoryl oxygen. Included in Table I are the unexpectedly high P=O stretching frequencies of some bicyclic phosphates compared to the more normal values observed for analogous open-chain compounds. Wagner[9] has esti-

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(5) O. C. Dermer and P. W. Solomon, *J. Am. Chem. Soc.*, **76**, 1697 (1954).

(6) W. S. Wadsworth and W. D. Emmons, *ibid.*, **84**, 610 (1962).

(7) J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

(8) T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1960).

mated P=O bond orders in a series of phosphoryl compounds of the basis of an internally consistent LCAO–MO method. A plot of P=O stretching frequency *vs.* P=O π-bond order based on these calculations reveals that trimethyl phosphate possesses a P=O π-bond order of 1.0, whereas this bond order in bicyclic phosphates such as II and IV is 1.4. These results substantiate the argument that the unusually high π-bond order in II and IV is associated with a withdrawal of electron density from the oxygen atom into available d orbitals on phosphorus. On the basis of Burger's observation that a decreasing extractant power of organophosphorus compounds for uranyl nitrate follows an increase in P=O stretching frequency for the ligand,[10] our results are not surprising. However, it is not clear at this time why unusually high P=O stretching frequencies are observed for polycyclic phosphates as opposed to the lower values associated with open-chain phosphates.

It is worthy of note that the increment in moment from I to II as shown in Table III is 2.95 D,[11] whereas this increase from open-chain phosphites to phosphates is about 1.2 D. On the basis of the infrared evidence a smaller P=O link moment for II than for an open-chain phosphate might be expected. However, these increments are only *apparent* values for the P=O link moments since they include other contributions, such as changes in bonding of phosphorus to the alkoxy oxygens, which cannot be separately evaluated on the basis of the dipole moment data alone.[11] The results of an X-ray structural analysis of II and electron diffraction studies on the bicyclic phosphite $P(OCH_2)_3CH$ and trimethyl phosphite now in progress will undoubtedly shed some light on the question of the bonding of phosphorus in these compounds.

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[9] E. L. Wagner, *J. Am. Chem. Soc.*, **85**, 161 (1963).

[10] L. L. Burger, U. S. Atomic Energy Commission Report HW-44888, 1957.

[11] T. L. Brown, J. G. Verkade, and T. S. Piper, *J. Phys. Chem.*, **65**, 2051 (1961).

Correspondence

The Molybdenum–Hydrogen Distance in Dihydridodi-π-cyclopentadienylmolybdenum

Sir:

The nature of the metal–hydrogen bond and the M–H distance in transition metal hydride complexes have given rise to considerable discussion. The point in dispute is whether the M–H distance is abnormally short in some of these compounds, that is, much less than a sum of covalent radii. The work relevant to this dispute has recently been reviewed in detail,[1,2] and it has been shown that the original arguments for a short M–H distance are no longer valid. The available evidence suggests that a normal M–H distance, that is, a distance consistent with the ordinary radii sum rules, is characteristic of the transition metal hydride complexes. The recent X-ray structure determination[3] of $(\pi\text{-}C_5H_5)_2MoH_2$, which reports an Mo–H distance of 1.2 ± 0.3 A, is in disagreement with this conclusion. We therefore felt that a reexamination of Gerloch and Mason's data[3] was in order. We demonstrate below that it is not possible to locate the metal-bonded hydrogen atom from the published X-ray data on $(\pi\text{-}C_5H_5)_2MoH_2$. It is also shown that these data do not support the reported[3] differences in carbon–carbon bond lengths.

Analysis of Gerloch and Mason's X-Ray Scattering Data.—The magnitudes of 274 observed structure factors in the $\{h0l\}$, $\{h1l\}$, $\{hk0\}$, and $\{0kl\}$ zones, on the "absolute" scale ×50, are listed in Gerloch and Mason's Table III. Of these, $F(40\bar{2}) = 0$ and presumably was included in error; it was omitted from the following analysis. It is necessary, with such a group of F_o values, to choose the method of analysis with care in order to avoid introduction of serious error. Thus, the proportion of the total number of independent $F(hkl)$ contained in this table is too small for three-dimensional Fourier series to be used. Further, two-dimensional Fourier series, with either F_o or ΔF (used by Gerloch and Mason) as coefficients, are unreliable especially in projection down axes of 10 A or greater as in the present crystal. The method of least squares was therefore selected as that best suited for analysis of Gerloch and Mason's scattering data.

In the correct use of the least-squares method, each observation must be weighted by the inverse variance in that observation. For investigations in which direct[4] estimation of this variance is not possible, a recent study[5] has demonstrated the Hughes' scheme[6] of $\sigma(F) \propto 4|F_{\min}|$ for $|F| \leq 4|F_{\min}|$, and $\sigma(F) \propto |F|$ for $|F| > 4|F_{\min}|$ to be the most acceptable alternative of the various empirical weighting schemes. Accordingly, Hughes' empirical weights were used, taking $|F_{\min}| = 375$ and the proportionality constant as 0.1. The approach to unity of S in Table I may be regarded as a demonstration that these weights are close to being correct. Neutral atomic scattering factors for C and

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[1] A. P. Ginsberg, "Transition Metal Chemistry," Vol. 1, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1965, Chapter 3.

[2] J. A. Ibers, *Ann. Rev. Phys. Chem.*, **16**, 375 (1965).

[3] M .Gerloch and R. Mason, *J. Chem. Soc.*, 296 (1965).

[4] S. C. Abrahams, *Acta Cryst.*, **17**, 1327 (1964).

[5] S. C. Abrahams and J. M. Reddy, *J. Chem. Phys.*, **43**, 2533 (1965).

[6] E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).