Table III

Stability Constants for Aminocarboxylic Acid Complexes of Sm(III)

Ligand	log K_1	No.[a] of Rings	log K_1/ no. of rings
α-Picolinate	3.85	1	3.85
Iminodiacetate[b]	6.64	2	3.32
Dipicolinate[1]	6.94	2	3.47
Nitrilotriacetate[c]	11.53	3	3.84
N-Hydroxyethylenediaminetriacetate[c]	15.28	4	3.82
Ethylenediaminetetraacetate[c]	17.14	5	3.43
1,2-Diaminecyclohexanetetraacetate[c]	18.63	5	3.73

[a] Assuming nitrogen is involved in the chelation. [b] L. C. Thompson, *Inorg. Chem.*, 1, 490 (1962). [c] T. Moeller, "The Chemistry of the Lanthanides," Reinhold Publishing Corp., New York, N. Y., 1963, p. 57.

as a donor atom in chelation to calculate the log K/(no. of rings), we have listed stability constant data for a number of aminocarboxylic acids systems in Table III. Again, the similar values of log K/(no. of rings) would seem to support the model involving nitrogen in the chelation of these complexes. It should be noted that the log K values in Table III were, however, not all obtained at the same ionic strength.[9]

The α-picolinate anion is approximately a hundredfold more basic than the N-oxide anion as indicated by their acid dissociation constants. This would lead us to expect that chelates of the former will be considerably more stable. In addition, the fact that the α-picolinate anion forms a five-membered ring compared to the six-membered ring with the N-oxide anion also predicts greater stability for the α-picolinate complexes.[7] Although we cannot predict quantitatively the differences to be expected in the stability constants for the complexes of the two ligands based on such differences in basicity and ring size, it seems probable that they would be larger than the observed differences. As a result, we might conclude that when all other factors are similar, chelation involving two oxygen atoms is more favored than chelation involving an oxygen and a nitrogen atom. On the other hand, comparison of the stability constants reported by Grenthe and Tobiasson[10] for diglycolate complexes (*e.g.*, log K_1 (Sm) = 3.54) and by Thompson[10] for iminodiacetate complexes (*e.g.*, log K_1 (Sm) = 6.64) indicates that just the opposite is true. The apparent conflict between these sets of data perhaps reflects the differences in the donor properties of an oxygen atom involved in an ether linkage and one involved in the N-oxide structure.

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[9] Subsequent to the original submission of this note, L. C. Thompson has reported the stability constants of the lanthanide α-picolinate complexes at an ionic strength of 0.1 *M* [*Inorg. Chem.*, **3**, 1319 (1964)]. For Sm, log K_1 = 4.06.

[10] I. Grenthe and I. Tobiasson, *Acta Chem. Scand.*, **17**, 2101 (1963).

Contribution from the Lake Charles Chemical Research
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Zerovalent Nickel Complexes. I. Synthesis of Tetrakis Nickel(0) Complexes

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Several compounds of the type $Ni(PY_3)_4$ have been prepared in recent years by the reaction of nickel tetracarbonyl[1-3] or other $Ni(PY_3)_4$ compounds[1,2] with trivalent phosphorus compounds. Their preparation by the direct reaction of nickel with trivalent phosphorus compounds has been reported in two instances,[4,5] and both of these under rather vigorous conditions.

We wish to report a facile synthesis of compounds of the type $Ni(PY_3)_4$ which circumvents the use of the highly toxic nickel carbonyl and allows isolation of the tetrakis complexes in high purity and yield.

The reaction has been effected by several techniques, the best of which involves heating a mixture of a trialkyl or triaryl phosphite with nickelocene ($C_{10}H_{10}Ni$) or dimethylnickelocene ($C_{12}H_{14}Ni$) in the absence or in the presence of a solvent. A temperature of 80° has been found satisfactory. Under these conditions the reaction proceeds rapidly and the resultant tetrakis complex can be readily isolated by precipitation with a polar solvent. The conversion of nickelocene or dimethylnickelocene is quantitative and the yields of tetrakis complex are high. Substitution of dimethylnickelocene for nickelocene results in a high yield of tetrakis complex. Dimethylnickelocene in soluble in the reaction media, whereas nickelocene is somewhat insoluble.

Experimental[6]

All complexes were formed by direct reaction of nickelocene or dimethylnickelocene and the pure ligand. The preparation could also be effected using a solvent, such as benzene, cyclohexane, ethylcyclohexane, cyclohexene, or other hydrocarbons. The complexes were precipitated by the addition of a polar solvent, such as methanol or acetone, washed with the precipitating solvent, and air dried. The complexes prepared by this technique are listed below.

Tetrakis[triphenyl phosphite]nickel(0), white powder, m.p. 146–148°; 96% yield. *Anal.* Calcd. for $C_{72}H_{60}O_{12}P_4Ni$: C, 66.53; H, 4.65; Ni, 4.52. Found: C, 66.59; H, 4.77; Ni, 4.66.

Tetrakis[tri(2-chloroethyl) phosphite]nickel(0), white crystals, m.p. 138–140°; 98% yield. *Anal.* Calcd. for $C_{24}H_{48}O_{12}Cl_{12}P_4Ni$: C, 25.36; H, 4.26; Cl, 37.43. Found: C, 26.27; H, 4.29; Cl, 37.18.

Tetrakis[tri(*p*-methoxyphenyl) phosphite]nickel(0), yellow powder, m.p. 98–100°; 33% yield. *Anal.* Calcd. for $C_{84}H_{84}O_{24}P_4Ni$: Ni, 3.54. Found: Ni, 3.30.

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[1] J. W. Irvine, Jr., and G. Wilkinson, *Science*, **113**, 742 (1951).

[2] G. Wilkinson, *J. Am. Chem. Soc.*, **73**, 5501 (1951).

[3] G. Wilkinson, *Z. Naturforsch.*, **9b**, 446 (1954).

[4] L. D. Quin., *J. Am. Chem. Soc.*, **79**, 3681 (1957).

[5] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

[6] Microanalysis for carbon and hydrogen by Galbraith Microanalytical Laboratories; nickel analysis by Columbian Carbon Analytical Division.

Tetrakis[tri(2-ethoxyhexyl) phosphite]nickel(0), white powder, m.p. 112–115°; 35% yield. *Anal.* Calcd. for $C_{96}H_{204}O_{24}P_4Ni$: Ni, 3.06. Found: Ni, 3.18.

Tetrakis[tri*p*(-tolyl) phosphite]nickel(0), white powder, m.p. 98–100°; 23% yield. *Anal.* Calcd. for $C_{84}H_{84}O_{12}P_4Ni$: Ni, 4.00. Found: Ni, 4.18.

Tetrakis[tri(2-ethylhexyl) phosphite]nickel(0), white powder, m.p. 112–115°; 48% yield. *Anal.* Calcd. for $C_{96}H_{204}O_{12}P_4Ni$: Ni, 3.4. Found: Ni, 3.3.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Photochemistry of Aqueous Octacyanomolybdate(IV) Ion, $Mo(CN)_8^{-4}$

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Received August 24, 1964

We report here the results of some investigations on the photolytic chemistry of aqueous $K_4Mo(CN)_8$ which seem to clarify some aspects of the rather complex behavior that is encountered. Earlier work in this laboratory[2] showed that exchange with $C^{14}N^-$, negligible in the dark, was strongly photocatalyzed. The quantum yield for the exchange was at least unity.[3] A later study[4] showed that irradiation produced free cyanide ion with a quantum yield at 370 mμ also of about unity. Low intensity irradiation eventually converted the yellow initial solution to one of a blue product, B, while tenfold higher intensities, of the order of 6 × 10^{-5} einstein/min. $cm.^2$, produced a transient red species, R. Subsequently Jakob and co-workers[5] have published a suggestion that R is the decacoordinated species $Mo(CN)_8(H_2O)_2^{-4}$. While our own studies were incomplete, they were extensive, and suggest a quite different formulation.

The preparation of $K_4Mo(CN)_8$ was as previously described.[2] The equipment and procedures for the photochemical work were also essentially the same as reported earlier.[4] The spectral changes that occur on irradiation of aqueous $Mo(CN)_8^{-4}$ ion using low light intensities are shown in Figure 1. Gaussian analysis[6] of the absorption spectrum of these solutions shows peaks at 510, 431, 368, 308, 267, and 240 mμ, of which the first two appear in Figure 1, and tentative assignments of these transitions have been made. Note that we find the third band at 368 mμ rather than at 376 mμ as reported by Jakob, *et al.*[5] The absorption spectrum of the blue product shows, in addition to the weak band at 615 mμ displayed in Figure 1, shoulders at 305 and 270 mμ, and a very high intensity peak at 223 mμ.

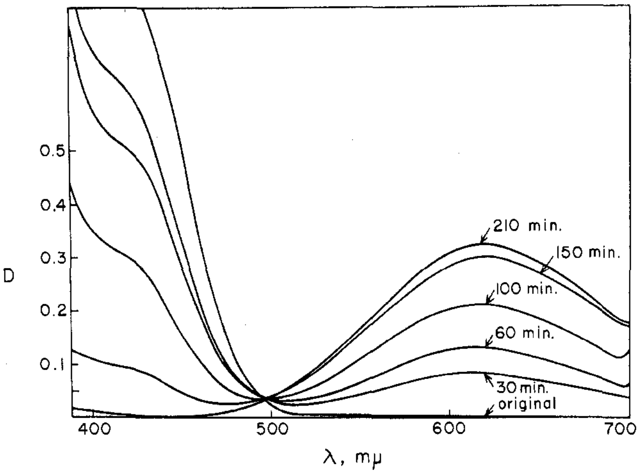

Figure 1.—Optical density for 1-cm. light path; solutions allowed to stand until red form had disappeared.

The terminal blue product, B, was isolated by fractional precipitation with ethanol and analyzed. *Anal.* Calcd. for $K_3Mo(CN)_4(OH)_3(H_2O)$[7]: C, 12.4; H, 1.3; K, 30.3; Mo, 24.8; N, 14.5, O, 16.6. Found: C, 11.5; H, 0.9; K, 29.4; Mo, 26.2; N, 14.7; O (by difference), 17.3. We thus disagree with Jakob, *et al.*,[5] who proposed $K_2Mo(CN)_4(OH)_2$. Not only are the analyses different (their formulation gives C, 15.4; H, 0.64; K, 25.0; Mo, 30.8; N, 17.9), but their species would presumably be octahedral in geometry and for a d^2 system, paramagnetism should be observed. We found B to be diamagnetic. Also, the intensity of the 610 mμ band (ε 35 l. $mole^{-2}$ $cm.^{-1}$) indicates a spin-allowed transition, yet for an octahedral complex the first spin-allowed process should occur at a much higher energy. An illustration would be the case of trivalent vanadium.[6] We are agreed, however, that the terminal blue product has four cyanides per molybdenum; it is possible that conditions of isolation and drying, if sufficiently extreme, could lead to loss of KOH and water.

The quantum yield for production of B was determined as follows, for light of 363 mμ (±5 mμ window width of the interference filter). At this wave length B absorbs negligibly, but since the solution was optically dense with respect to $Mo(CN)_8^{-4}$, it was necessary to allow for the varying degree of absorption of incident light during the course of the photolysis. If the absorption coefficient, a, be defined as $I/I_0 = \exp(-aC)$, then, for a first-order photolysis reaction

$$a(C_0 - C) - \ln\left[\frac{1 - e^{-aC}}{1 - e^{-aC_0}}\right] = (\varphi I_0 a/V)t = k't \quad (1)$$

where φ is the quantum yield, V, the volume of solution,

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[1] This report is based on portions of the junior author's Ph.D. dissertation.

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[3] J. P. Welker, Ph.D. Dissertation, University of Southern California, 1950.

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[7] N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. II, Oxford Press, 1950, p. 1056.