TABLE III

OBSERVED INFRARED ABSORPTION BANDS (CM.$^{-1}$) OF THE METHANESULFONATE ION AND SOME TENTATIVE ASSIGNMENTS

$AgCH_3SO_3$	KCH_3SO_3	Tentative assignment
3027, 3012 w	3000, 3010, w	ν_7
2938, 2920 w	2945 sh, 2925, m	ν_1
2948 vw	2845 w	$2\nu_9$
1437, 1418	1433, 1420 w	ν_9
1343, 1321 m	1335 m	ν_4
1195 b, vs 1130 b, s	~1200, vs, b	ν_8
1030 m	1056, 1048 s	ν_2
772 m	787, 773 m	ν_{11}
560 sh		ν_5, ν_{10} (and ν_3?)
554 s	563 s	
548 sh	558 sh	
530 s	538 s	
518 s	528 s	

appears to show that the upper band is due to the degenerate mode. The absorption in the 500–600 cm.$^{-1}$ region must be due principally to SO_3 deformations. The position of the C–S stretching frequency remains uncertain; such modes are known to be usually weak, and in this case it may be obscured by the strong SO_3 deformation bands. The libration and the SO_3 rocking modes would be expected to have frequencies below the range of our observations.

For the two $CH_3SO_3^-$ compounds of Mo_6Cl_8, the spectra are entirely consistent with the assumption that each $CH_3SO_3^-$ ion becomes attached through one oxygen atom to a molybdenum atom. The bonds from sulfur to the two uncoordinated oxygen atoms acquire greater double bond character and give rise to symmetric and antisymmetric S–O stretching modes at ~1280 and ~1150 cm.$^{-1}$; the mean of these frequencies, 1215 cm.$^{-1}$, is higher than the mean of the two frequencies, ~1130 cm.$^{-1}$, for the uncoordinated $CH_3SO_3^-$ ion, but the frequencies are not quite so high as those in sulfones (typically ~1150, ~1320 cm.$^{-1}$) where the S–O bond orders should be higher. At the same time the frequency of the S to coordinated O bond, which should decrease slightly in bond order, is in the range 950–1000 cm.$^{-1}$. In the DMF compound there is a strong doublet, 980, 950 cm.$^{-1}$, which may be so assigned with certainty. In the DMSO compound both the S–O stretch of $CH_3SO_3^-$ and strong DMSO absorption occur in the 900–1000 cm.$^{-1}$ region. Tentatively, we assign the S–O stretch of $CH_3SO_3^-$ to one or both of the bands at 982 and 997 cm.$^{-1}$ and the S–O stretch of DMSO to one of the bands at 915 and 950 cm.$^{-1}$.

Summary of Infrared Results.—In all six compounds, there is direct evidence that six ligands are bound to each $[Mo_6Cl_8]^{4+}$ ion. For the perchlorate compounds, the spectra show that the perchlorate ions are free; however, there are six DMF or DMSO molecules present and the spectra contain only bands which are attributable to these molecules when they are coordinated through oxygen. For the $[Mo_6Cl_{12}L_2]$ compounds, the spectra again show the presence of bound DMSO or DMF and the absence of any free molecules of these substances. Presumably, the six ligands held by $[Mo_6Cl_8]^{4+}$ in these cases are 4Cl + 2L, L = DMSO or DMF. Finally, for the methanesulfonate compounds, the infrared spectra show the absence of any uncoordinated ligands or anions, the presence of DMF or DMSO coordinated through oxygen, and the presence of $CH_3SO_3^-$ ions coordinated through one oxygen.

The preference of $[Mo_6Cl_8]^{4+}$ for the oxygen rather than the sulfur atom of DMSO is an indication that it has the properties of a class (a) rather than a class (b) acceptor.[15] It has previously been found[14] that the typical class (b) species Pt(II) and Pd(II) prefer sulfur while many metal ions of class (a) prefer oxygen in DMSO.

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[15] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 256 (1958).

Notes

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Complexes of the Lanthanide Elements with α-Picolinate and α-Picolinate N-Oxide Ions

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In a study of the dipicolinate complexes of the lanthanide elements, Grenthe and Fernelius[1] concluded that the heterocyclic nitrogen atom is not involved in the chelate ring structure. Since it seems rather well established[2,3] that the variation in stability constant with atomic number of the lanthanides differs for monodentate compared to bidentate complexing, a study of the stability constants of α-picolinate complexes could provide clearer evidence of the role of the nitrogen atom in these complexes. The complexes of α-picolinic acid N-oxide were also studied to assess the role of ring size and nitrogen *vs.* oxygen as donor atoms (Figure 1).

Experimental

Reagents and Equipment.—Lanthanide perchlorate solutions were prepared and standardized by a procedure that has been

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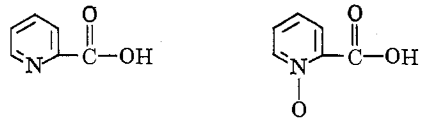
[1] I. Grenthe and W. C. Fernelius, "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, p. 12.

[2] J. L. Bear, G. R. Choppin, and J. V. Quagliano, *J. Inorg. Nucl. Chem.* **25**, 513 (1963).

[3] W. R. Stagg and J. E. Powell, *Inorg. Chem.*, **3**, 242 (1964).



α-Picolinic acid α-Picolinic acid N-oxide

Figure 1.

TABLE I

SUMMARY OF DATA

Metal ion	Total metal concn., mM	pH range	No. of data points	Maximum $\bar{n}$ attained
		α-Picolinates		
La	8.23	3.45–4.98	17	3.01
Ce	10.13	2.57–5.05	18	1.77
Pr	12.00	3.55–4.93	18	2.47
Nd	9.93	3.23–4.93	17	2.39
Sm	8.54	3.50–5.02	18	2.54
Eu	7.94	3.61–5.05	18	2.31
Gd	8.25	3.58–5.00	18	2.81
Dy	9.01	3.31–4.99	18	2.69
Tm	8.90	2.89–5.03	16	2.26
Yb	8.18	3.17–5.03	18	2.46
Lu	8.38	2.70–5.05	16	2.14
		α-Picolinate N-Oxides		
La	4.11	3.01–3.27	8	0.69
Ce	5.07	3.03–3.26	7	0.67
Pr	6.00	2.95–3.28	11	0.78
Nd	4.96	2.86–3.26	15	0.83
Eu	5.09	2.51–3.28	12	0.92
Gd	4.13	3.03–3.26	16	0.99
Dy	4.51	2.99–3.27	17	0.87
Tm	4.45	2.71–3.23	16	1.22
Yb	4.09	2.78–3.24	16	1.23
Lu	4.21	2.67–3.23	10	1.20

described previously.[4] Sodium perchlorate (G. F. Smith Co., anhydrous reagent grade) was used in adjusting all solutions to 2.0 M ionic strength. This medium was chosen to facilitate comparisons with the results of previous investigations in this laboratory. Acid buffer solutions were prepared by half-neutralizing a standard acid solution so that the buffer ratio was approximately unity. The acids used were obtained from Bios Laboratories, New York, N. Y.

A Beckman Model G pH meter was used with a Beckman Type 42 glass electrode and a silver–silver chloride reference electrode.

Procedure.—The method of Bjerrum, as described previously,[4,5] was used to evaluate the first (K_1) and the second (K_2) complex stability constants. The procedure consisted in titrating with an acid buffer solution two solutions, one containing metal ions and $NaClO_4$, the other only $NaClO_4$. Both solutions had an ionic strength of 2.0 M and were maintained at 25.0 ± 0.1° in a water-jacketed cell during the titration. From the pH values recorded upon the addition of each increment of titrant, the concentration of free ligand, [L], and the average number of ligands bound per metal ion, $\bar{n}$, were calculated. Table I summarizes the results of the various titrations.[6] The appropriate values of $\bar{n}$ and [L] were used to calculate the first and second stability constants as described in a previous publication.[7]

Discussion

Table II lists the values of the log of the stability constants K_1 and K_2 where $K_i = [\mathrm{M}_i]/[\mathrm{ML}_{i-1}][\mathrm{L}]$. Error limits were estimated from maximum and minimum values of $\bar{n}$ and [L] obtained by variation within the determinate error of the data. The error limits were found to be ±10% for K_1 and ±20% for K_2.

In order to facilitate the interpretation of the data, the acid dissociation constants of the two acids were obtained by titration with base for solutions of 2.0 M ionic strength. These values were 4.58×10^{-6} for α-picolinic acid and 4.85×10^{-4} for α-picolinic acid N-oxide. The error limits for these determinations were ±10% in both cases.

TABLE II

STABILITY CONSTANTS

(25.0° and 2.00 M Ionic Strength)

Metal ion	α-Picolinate		α-Picolinate N-oxide	
	log K_1	log K_2	log K_1	log K_2
La	3.50 (±0.05)	2.39 (±0.08)	2.53 (±0.05)	1.76 (±0.08)
Ce	3.63	2.10	2.71	...
Pr	3.62	2.63	2.75	2.26
Nd	3.79	2.86	2.91	2.15
Sm	3.85	2.99	...	...
Eu	3.80	2.93	2.94	2.29
Gd	3.77	3.07	2.93	2.27
Dy	3.83	3.09	3.00	2.55
Tm	4.31	3.17	3.16	2.69
Yb	4.28	3.38	3.15	2.60
Lu	4.54	3.11	3.48	2.84

The variations in the stability constants with increasing atomic number indicate that both of these ligands form chelate complexes with the lanthanide ions. This is inferred from the similarity of the stability constant variations to those of known chelate systems[3,4,7] in which the stability constants increase from La to Lu. In contrast, the stability constants with monodentate ligands have a maximum value around Sm.[2,3] In a recent study of lanthanide complexes of aminocarboxylic acids, Thompson similarly concluded that the aliphatic nitrogen is involved in chelation.[8] Using the assumption that nitrogen acts

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[4] G. R. Choppin and J. A. Chopoorian, *J. Inorg. Nucl. Chem.*, **22**, 97 (1961).

[5] J. L. Bear, G. R. Choppin, and J. V. Quagliano, *ibid.*, **24**, 1601 (1962).

[6] The data for each individual titration have been deposited as Document No. 8141 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting $3.75 for photoprints, or $2.00 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[7] H. Yoneda, G. R. Choppin, J. L. Bear, and J. V. Quagliano, *Inorg. Chem.*, **3**, 1642 (1964).

[8] L. C. Thompson, *ibid.*, **3**, 1015 (1964).

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-Hydroxyethylene-diaminetriacetate[c]	15.28	4	3.82
Ethylenediamine-tetraacetate[c]	17.14	5	3.43
1,2-Diaminecyclo-hexanetetra-acetate[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.

Acknowledgments.—We wish to acknowledge the financial support of the U.S.A.E.C. through Contract AT-(40-1)-1797. The N.S.F. also provided support through its grant to the F.S.U. Computing Center.

(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).

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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.