8-layer repetition scheme would lead to a 24-layer cell.

Other hypotheses to account for the superlattice can be advanced. These hypotheses are being examined.

Acknowledgments.—The IBM 1620 Fourier programs were written by D. Hall of the University of Pittsburgh and modified for use on the University of Connecticut computer by R. D. Rosenstein of the University of Pittsburgh. The Computer Center of the University of Connecticut is supported in part by grant GP-1819 of the National Science Foundation.

Assistance for the crystallographic portions of this work was provided by the National Science Foundation through grant GP 1396. J. M. L. held a National Science Foundation Cooperative Summer Fellowship. This support is gratefully acknowledged.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

Some New Derivatives of the Octa-μ_3-chlorohexamolybdate(II), $[Mo_6Cl_8]^{4+}$, Ion[1]

BY F. A. COTTON AND N. F. CURTIS

Received October 6, 1964

Attempts to prepare new compounds in which the six centrifugally directed Mo orbitals of $[Mo_6C_8]^{4+}$ are occupied by various ligands are described. Only in relatively few cases were stoichiometrically well-defined products obtained. These products were: $[Mo_6Cl_8L_6](ClO_4)_4$, $[Mo_6Cl_8L_2(CH_3SO_3)_4]$, and $[Mo_6Cl_{12}L_2]$, where L, in each type of compound, is either $(CH_3)_2SO$ or $HCON(CH_3)_2$. The infrared spectra of these compounds have been studied and the assignments show that the ClO_4^- ions do not become coordinated while all $(CH_3)_2SO$ and $HCON(CH_3)_2$ molecules and the $CH_3SO_3^-$ ions are coordinated to Mo atoms through their oxygen atoms. From the composition and infrared evidence regarding coordination, it appears that in all cases the Mo_6Cl_8 group binds just six additional ligands.

Introduction

The preparation of compounds containing molybdenum and tungsten in the formal oxidation state of II was first reported by K. Lindner and co-workers in the early 1920's.[2] The X-ray work of Brosset[3] established the presence of the unit $[Mo_6Cl_8]^{4+}$ in these compounds. More recent chemical studies by Sheldon[4] have shown that this $[Mo_6Cl_8]^{4+}$ ion is a persisting species which binds up to six additional donors (halide ions, water or amine molecules, etc.), presumably by means of the six centrifugally directed orbitals of the molybdenum atoms. The electronic structure of the $[Mo_6Cl_8]^{4+}$ ion has been treated on a molecular orbital basis by Crossman, Olsen, and Duffey[5] and by Cotton and Haas.[6] The presence of an empty, centrifugally directed, σ-orbital on each molybdenum atom is indicated by these MO treatments.

The related questions of the ability of these orbitals to bind electron pair donors, and the types of donors which might be preferred, naturally arise. While previous work[3,4] has shown that binding of additional ligands in these positions does occur, it seemed of interest to extend this line of enquiry using other ligands, especially those which can indicate by their infrared spectra the manner and strength of their attachment. This paper reports some results of such a study.

Experimental

Hexamolybdenum dodecachloride, Mo_6Cl_{12}, was prepared by a method which was essentially that of Sheldon.[4] The yield, based on molybdenum, was improved by having excess molybdenum in the long Vycor tube and passing the $MoCl_4$ over red hot molybdenum in a stream of nitrogen. The excess molybdenum was conveniently recovered when the Mo_6Cl_{12} was dissolved in hydrochloric acid.

Analyses for molybdenum were carried out by decomposing samples in ammoniacal peroxide solution and precipitating as lead molybdate. Other analytical results were obtained by S. M. Nagy, M.I.T.

$Mo_6Cl_{12}(DMF)_2$.[7]—Mo_6Cl_{12} was dissolved in a small volume of warm DMF. The solution was filtered and the product precipitated by slow addition of 2-propanol. Alternatively, the Mo_6Cl_{12} was dissolved in absolute ethanol, the solution filtered, and the product caused to precipitate by addition of a slight excess of DMF. The product was filtered, washed well with ethanol, then ether, and dried under vacuum.

Anal. Calcd. for $C_6H_{14}Cl_{12}Mo_6N_2$: C, 6.46; H, 1.27; N, 2.51; Mo, 51.61. Found: C, 6.20; H, 1.37; N, 2.26; Mo, 49.7.

$Mo_6Cl_{12}(DMSO)_2$.[7]—This was prepared in the same way as the DMF compound, using DMSO in place of DMF.

Anal. Calcd. for $C_4H_{12}Cl_{12}Mo_6O_2S_2$: C, 4.15; H, 1.05; Mo, 49.74. Found: C, 4.15; H, 1.12; Mo, 50.0.

$[Mo_6Cl_8(DMF)_6](ClO_4)_4$.—$Mo_6Cl_{12}$ (1 g.) was dissolved in 10 ml. of methanol and the solution added to a solution of 0.82 g. of $AgClO_4$ in 10 ml. of methanol. The mixture was stirred well and left to stand in the dark with intermittent agitation for 30 min. The precipitated AgCl was filtered off and washed several times with 1-ml. portions of methanol. DMF (1 ml.) was added to the combined liquors, and the precipitated product was filtered

---

[1] This work has been supported by the U. S. Atomic Energy Commission.

[2] *Cf.* N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, 1950, Vol. II, pp. 1061–1066, for a summary of the literature up to 1946.

[3] C. Brosset, *Arkiv. Kem. Min. Geol.*, **20A**, No. 7 (1945); **22A**, No. 11 (1946).

[4] J. C. Sheldon, *J. Chem. Soc.*, 1007, 3106 (1960); 4183 (1963); 1287 (1964).

[5] L. D. Crossman, D. P. Olsen, and G. H. Duffey, *J. Chem. Phys.*, **38**, 73 (1963).

[6] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).

[7] In this paper DMF represents dimethylformamide and DMSO represents dimethyl sulfoxide.

off, washed well with 2-propanol, then ether, and dried under vacuum. Alternatively, the labile chloride can be precipitated from a DMF solution of Mo_6Cl_{12} and the product then precipitated by addition of 2-propanol.

Anal. Calcd. for $C_{18}H_{42}Cl_{12}N_6Mo_6O_{22}$: C, 12.75; H, 2.50; N, 4.95; Mo, 33.95. Found: C, 12.6; H, 2.47; N, 4.82; Mo, 33.9.

Caution! The dried material was sometimes *very* shock-sensitive and detonated with *much* violence. For safety, the product should be separated into small portions before drying and it should not be dried on a fritted glass disk as this appears to enhance its sensitivity.

$[Mo_6Cl_8(DMSO)_6](ClO_4)_4$.—This was prepared in the same manner as the corresponding DMF compound. The explosive properties of this compound are similar to those of the DMF derivative.

Anal. Calcd. for $C_{12}H_{36}Cl_{12}Mo_6O_{22}S_6$: C, 8.35; H, 2.10; Cl, 16.43; Mo, 33.35. Found: C, 8.23; H, 2.1; Cl, 16.4; Mo, 33.5.

$[Mo_6Cl_8(DMF)_2(CH_3SO_3)_4]$.—$Mo_6Cl_{12}$ (1 g.) was dissolved in 10–20 ml. of warm DMF and 0.81 g. of $AgCH_3SO_3$ added to the cold solution. The mixture was stirred and left to stand for 30 min. with occasional agitation. The precipitated silver chloride was removed by filtration, and 2-propanol was added slowly, with stirring, to the filtrate to precipitate the product, which was filtered off, washed well with 2-propanol and ether, and dried under vacuum.

Anal. Calcd. for $C_{10}H_{26}Cl_8Mo_6N_2O_{12}S_4$: C, 8.67; H, 1.89; N, 2.02; Mo, 41.45. Found: C, 9.02; H, 1.83; N, 2.05; Mo, 41.3.

$[Mo_6Cl_8(DMSO)_2(CH_3SO_3)_4]$.—This was prepared in the same way as the corresponding DMF compound.

Anal. Calcd. for $C_8H_{24}Cl_8Mo_6O_{14}S_6$: C, 6.88; H, 1.73; Mo, 41.24. Found: C, 6.96; H, 1.73; Mo, 41.2.

Attempted Preparation of Other Compounds.—It has been reported[2] that the addition of alcoholic silver nitrate to an alcoholic solution of Mo_6Cl_{12} causes precipitation of one-third of the chloride as silver chloride and that the compounds $(Mo_6Cl_8)(NO_3)_4$ and $(Mo_6Cl_8)(NO_3)_4(C_2H_5OH)_2$ (formulated as trimeric Mo_3Cl_4 species) were isolated from the filtrate. Attempts to repeat this experiment were not successful. Addition of an alcohol-soluble silver salt to an alcohol solution of Mo_6Cl_{12} causes initial precipitation of yellow material containing silver and molybdenum, apparently $Ag_2Mo_6Cl_{14}\cdot n$ROH. When silver perchlorate or silver methyl sulfonate is added in excess the initial precipitate redissolves and one-third of the chloride is precipitated as silver chloride, leaving a clear yellow solution. With silver nitrate in excess, the molybdenum remains in the precipitate, which is dark in color, probably indicating some decomposition of the $[Mo_6Cl_8]^{4+}$ group. The same results were obtained in DMF[7] or DMSO[7] solution, one-third of the chloride precipitating as silver chloride with silver perchlorate or silver methyl sulfonate, while with silver nitrate a vigorous reaction occurred, with evolution of oxides of nitrogen and apparent disruption of the $[Mo_6Cl_8]^{4+}$ system.

Upon evaporating the methanol solution obtained after precipitation of the labile chloride ion of Mo_6Cl_{12} with $AgClO_4$, an extremely shock-sensitive yellow powder was obtained. Because of its extreme sensitivity, little effort was made to characterize it, but the infrared spectrum showed the presence of perchlorate ions and organic material and it may be $[Mo_6Cl_8(CH_3OH)_6](ClO_4)_4$.

Addition of aliphatic amines to the methanol solution from which labile chloride had been removed caused the formation of orange precipitates which rapidly changed to dark brown, presumably with disintegration of the $[Mo_6Cl_8]^{4+}$ group. Pyridine (or quinoline, etc.) caused the formation of an orange precipitate. This, when filtered, washed well with methanol and ether, and sucked dry had an analysis corresponding *approximately* to $[(Mo_6Cl_8)(py)_2](ClO_4)_4$. Under vacuum the pyridine was slowly lost. The initial material detonated extremely violently if heated. As the pyridine was pumped off under vacuum the substance became *extremely* shock-sensitive, although the resulting explosion became less violent as the amount of organic matter decreased.

With some other compounds, *i.e.*, pyridine N-oxide, triphenylphosphine oxide, triphenylarsine oxide, dibenzyl sulfoxide, yellow amorphous precipitates were obtained. Analytical figures were erratic and in poor agreement with any stoichiometric formulas. The results could usually be explained by the formation of mixtures of products of the type $[(Mo_6Cl_8)L_n(MeOH)_{6-n}](ClO_4)_4$, where L is the neutral ligand and n is somewhat variable, depending on the exact mode of preparation and the identity of L. The products were always amorphous, and attempts at recrystallization were not successful. The substances were all violently explosive.

Triphenylphosphine and triphenylarsine caused no precipitation from the $[Mo_6Cl_8](ClO_4)_4$ solution in methanol.

Discussion

To summarize the preparative part of this work, it may be said that the number of ligands which may attach themselves to the $[MoCl_8]^{4+}$ group to give pure, well-defined compounds appears to be more limited than one might expect. There is, of course, the possibility that there exist reaction conditions and techniques other than those we have used which will permit the isolation of compounds which were not successfully prepared in the present study.

Only three sorts of compounds were obtained in analytically satisfactory condition, namely, $Mo_6Cl_{12}L_2$, where L = DMSO or DMF, obtained by addition of DMSO or DMF to Mo_6Cl_{12} in solution; $[Mo_6Cl_8L_6](ClO_4)_4$, obtained by addition of DMSO or DMF to solutions of Mo_6Cl_{12} from which the four labile chloride ions had been removed using $AgClO_4$; and $[Mo_6Cl_8L_2(CH_3SO_3)_4]$, obtained by adding DMSO or DMF to solutions of Mo_6Cl_{12} from which the labile chloride ions had been removed with $AgCH_3SO_3$.

Infrared Spectra.—The infrared spectra of the analytically pure compounds provide information about the binding of DMSO, DMF, and $CH_3SO_3^-$ to the $[Mo_6Cl_8]^{4+}$ ion. Table I lists the various absorption bands to be discussed.

Perchlorate Spectra.—In both of the compounds containing perchlorate ions, the infrared spectra show that the perchlorate ions are excluded from coordination. A study of the effects of coordination upon the infrared spectrum of this ion has been described by Hathaway and Underhill.[8] The unperturbed perchlorate ion has four fundamental modes whose nature, symmetry, and approximate typical frequencies, in cm.$^{-1}$, are as follows: ν_1, Cl–O str., a_1, 935; ν_2, O–Cl–O def., e, 460; ν_3, Cl–O str., t_2, 1060; ν_4, O–Cl–O bend, t_2, 630.

The major effects of attaching the perchlorate ion to a metal ion through one oxygen atom should be to confer some infrared activity upon ν_1 and alter its frequency somewhat; to make ν_2 somewhat infrared active as well as to split it and shift the frequency; to split or greatly broaden the inherently infrared-active t_2 modes. None of these effects is observed in the two compounds under consideration. In each case ν_4 appears at 618 cm.$^{-1}$ as a very sharp, symmetrical band, while ν_3 appears at 1075–1085 cm.$^{-1}$ and is neither split

---

(8) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

TABLE I

INFRARED ABSORPTION BANDS OF THE COMPLEXES

Compound	Absorption bands,[a] cm.$^{-1}$	Assignments or remarks
$[Mo_6Cl_8(DMSO)_6](ClO_4)_4$	1082 vs	ν_3 of ClO_4^-
	930 b, s	Mainly S–O str.
	717 w	C–S str.
	678 vw	
	618 m, vsp	ν_4 of ClO_4^-
	465 mw	Mo–O str.?
$[Mo_6Cl_8(DMF)_6](ClO_4)_4$	1640 s	C–O str. of DMF
	1370 m	DMF bands, slightly shifted by coordination
	1260 w	
	1235 w	
	1075 vs	ν_3 of ClO_4^-
	698 s	N—C=O bend of DMF
	618 m	ν_4 of ClO_4^-
	422 m	Mo–O str.
$[Mo_6Cl_{12}(DMSO)_2]$	~927 b, s	S–O str.
	715 w	C–S str.
	~670 vw	
	460 m	Mo–O str.?
$[Mo_6Cl_{12}(DMF)_2]$	1650 s	C–O str.
	1370 s	DMF bands, slightly shifted by coordination
	1245 w	
	1233 w	
	1110 mw	
	693 ms	N—C=O bend of DMF
	420 m	Mo–O str.?
$[Mo_6Cl_8(DMSO)_2(CH_3SO_3)_4]$	1277 vs	Sym. and asym. $>SO_2$ stretches of $CH_3SO_3^-$
	1150 vs	
	997 s	S–O str. of DMSO plus other DMSO absorption; S–O (coord.) str. of $CH_3SO_3^-$
	982 s	
	950 s	
	915 s	
	775	CH_3 rock (ν_{11}) of $CH_3SO_3^-$
	562 m	ν_5, ν_{10} of CH_3SO_3
	543 m	
	533 w	
	522 mw	
	480 m	Mo–O str.?
$[Mo_6Cl_8(DMF)_2(CH_3SO_3)_4]$	1650 s	C–O str. of DMF
	1280 vs	Sym. and asym. $>SO_2$ stretches of $CH_3SO_3^-$
	1150 vs	
	980 950 s	S–O (coord.) str.
	777 m	CH_3 rock (ν_{11}) of $CH_3SO_3^-$
	710 ms	N—C=O bend of DMF
	560 ms	ν_5, ν_{10} of $CH_3SO_3^-$
	542 w, sh	
	533 m	
	515 w	
	425 m	Mo–O str.?
	Absorption	

[a] s, strong; m, medium; w, weak; sh, shoulder; sp, sharp; v, very; b, broad.

nor broader than it is in various ionic compounds in which some degree of broadening occurs due simply to an environment of low symmetry. In the DMSO complex, there are no indications of the appearance of ν_1 or ν_2, but ligand bands at ~930 cm.$^{-1}$ (s, b) and 465 cm.$^{-1}$ (m) would be likely to mask them if they appeared weakly so that no conclusion can be drawn from this negative result. In the spectrum of the DMF complex the regions 900–950 and 450–500 cm.$^{-1}$ are sufficiently free of absorption due to the DMF ligand that any but the very weakest absorption due to the ν_1 and ν_2 bands of ClO_4^- would be discernible. No significant absorption is observed.

Spectra of DMF Compounds.—In all the DMF compounds, the spectra (Table I) afford conclusive evidence that DMF is coordinated through oxygen. Thus the C–O stretching frequency, which occurs at 1670 cm.$^{-1}$ in DMF itself, is lowered to 1640–1650 cm.$^{-1}$ in the complexes. The shifts, −20 to −30 cm.$^{-1}$, are quite comparable to those previously reported for O-coordinated DMF.[9–11] In addition, the newly discovered effect[12] of coordination on the N—C=O bending mode is clearly evident in each case.

TABLE II

GENUINE NORMAL VIBRATIONS FOR THE METHANESULFONATE ION, $CH_3SO_3^-$

Symmetry type (C_{3v})	Serial no.	Approximate description	Probable range, cm.$^{-1}$
A_1	ν_1	CH_3 str.	2800–3100
	ν_2	SO_3 str.	1000–1250
	ν_3	C–S str.	600–800
	ν_4	CH_3 def.	1300–1400
	ν_5	SO_3 def.	500–600
A_2	ν_6	Libration	<200
E	ν_7	CH_3 str.	2800–3100
	ν_8	SO_3 str.	1000–1250
	ν_9	CH_3 def.	1400–1500
	ν_{10}	SO_3 def.	500–600
	ν_{11}	CH_3 rock	700–900
	ν_{12}	SO_3 rock	<450

In each DMF compound there is a medium intensity band at 420–425 cm.$^{-1}$ which does not seem to have any assignment as a shifted DMF band. We suggest, without any positive evidence, however, that these bands may be assigned to Mo–O stretching.

Spectra of DMSO Compounds.—In all cases, the broad, intense band at ~1040 cm.$^{-1}$, due mainly to S–O stretching,[13] disappears completely. No new absorption is found at higher frequencies, as would be expected[14] if the attachment of DMSO were through the sulfur atom. Instead there is a considerable intensification in the complex pattern of absorption in the 900–950 cm.$^{-1}$ region, particularly at about 930 cm.$^{-1}$, which is indicative[14] of attachment of DMSO through the oxygen atom. As with the DMF compounds, a medium intensity band appears in the 460–480 cm.$^{-1}$ region, which may be an Mo–O stretching band.

Methanesulfonate Spectra.—In order to interpret the spectra of the compounds containing $CH_3SO_3^-$, it was first necessary to record and attempt to assign the spectrum of the $CH_3SO_3^-$ ion itself. Both the Ag^+ and the K^+ salts were used for this purpose. Table II gives a list of the expected normal vibrations of $CH_3SO_3^-$ and Table III records the bands observed and suggests assignments. All normal modes except ν_6 should be infrared active. In the KCH_3SO_3 spectrum, virtually every band is a doublet, suggesting that there are two crystallographically inequivalent sets of $CH_3SO_3^-$ ions. The assignments of the methyl group frequencies, ν_1, ν_4, ν_7, ν_9, $2\nu_9$, and ν_{11}, are routine. The assignments of ν_2 and ν_8 are also straightforward; a reversal of these two is disfavored by the splitting of the upper but not the lower band in the silver salt. This

---

(9) J. Archambault and R. Rivest, *Can. J. Chem.*, **36**, 1461 (1958).

(10) C. L. Rollinson and R. C. White, *Inorg. Chem.*, **1**, 281 (1962).

(11) M. A. J. Jungbauer, Ph.D. Thesis, University of Notre Dame, 1963. Shifts of −15 to −37 cm.$^{-1}$ are reported for 16 transition metal complexes of DMF. We thank Brother Columba Curran for informing us of these data prior to publication.

(12) M. A. J. Jungbauer and C. Curran, *Nature*, **202**, 290 (1964).

(13) W. D. Horrocks, Jr., and F. A. Cotton, *Spectrochim. Acta*, **17**, 134 (1961).

(14) F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960).

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	~1200, vs, b	ν_8
1130 b, s		
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.

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

Notes

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLORIDA

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

BY H. YONEDA, G. R. CHOPPIN, J. L. BEAR,
AND A. J. GRAFFEO

Received August 24, 1964

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

---

(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).