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Heteropoly Complexes of Lanthanum with Unsaturated Heteropolytungstate Ligands

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As a sequel to our earlier reports [1] of heteropolyanions containing heteroatoms of two elements we report here the complexes of the 11- and 17-series heteropolyanions [2–5] of the type $X^{n+}W_{11}O_{39}{}^{(12-n)-}$ and $X'_2W_{17}O_{61}{}^{10-}$ (where X = B, Si, Ge, As and X′ = P, As) with lanthanum. Previously complexes between certain lanthanides and polyanions of some of the aforementioned type have been described by Weakley and Peacock [6]. Our study dealt with the preparation, investigation of the pH range of stability, reactions and spectra of the complexes.

Experimental

The complexes could be synthesised by the following general methods.

Method 1

The parent acid of the 12- and the 18-series are isolated as the ether addition compound [7] which is mixed with water and gently heated to remove the ether. The method suggested by Peacock and Weakley [6] is then followed using $La(NO_3)_3$ instead of $Ce(NO_3)_3$. However, this method is not recommended for the syntheses of the complexes of the ligands* BW_{11} and AsW_{11} because of the difficulty of isolating the parent free acid as the etherates [7, 8] and also the low final yield.

Method 2

The method consists of generating the ligands *in situ* by reacting WO_4^{2-}, $X^{n+}O_4^{(8-n)-}$ in an appropriate pH range [3, 7, 8] and allowing it to react with La^{3+}. All the complexes of the 11-series ligands could be synthesised in this way but the method is specially suitable for the synthesis of the complexes $La(BW_{11})_2$ and $La(AsW_{11})_2$. A typical synthesis of potassium bis(11-tungstoboro)lanthanate(III) is described to illustrate the method. 100 g $Na_2WO_4\cdot 2H_2O$ (0.303 mol) is dissolved in 500 cm^3 of water and the pH adjusted to 6–6.5 with glacial acetic acid. About 10 g H_3BO_3 (0.162 mol; a large excess of boron but the calculated amount of the other heteroatoms are needed) in minimum quantity of water is added to the tungstate solution and the reaction mixture is refluxed for 30 minutes at 80–90 °C. A solution containing 6.50 g $La(NO_3)_3\cdot 6H_2O$ (0.015 mol) is added dropwise and the solution is cooled, filtered and treated with 50 g solid KCl and the reaction mixture refrigerated. The product which separates out is recrystallised from the minimum amount of warm water (70 °C). It may be noted that this method is not applicable to the synthesis of the complexes of the 17-series, since the ligands cannot be generated by this method [3]. As an alternative to the above procedure the ligands of the 11- and 17-series are isolated as the potassium salt [3, 7] and are reacted in solution with La^{3+}. However, method 1 is to be preferred over this one since it is difficult to isolate salts of the ligands BW_{11}, AsW_{11} and As_2W_{17}.

The salts of these heteropoly complexes with small cations such as K^+ are extremely soluble in water and are difficult to handle. However, the caesium and the guanidinium salts are readily obtained from the potassium salts by metathetical reactions and are easily recrystallisable.

Lanthanum and the other elements were analysed according to the methods described elsewhere [1, 6, 8].

Results and Discussion

For both types of complexes ion-exchange studies show that the lanthanum is in the anion. The analytical results (Table) show that $La(XW_{11})_2$ and $La(X_2W_{17})_2$ types of complexes are formed between the ligand and the metal. Thus the complexes belong to the series reported earlier by Peacock and Weakley [6] which in turn is related to the triheteropolyanions initially reported by Baker and coworkers [9, 11]. Their arguments regarding the probable structure of the anions, their relation to the Keggin and Dawson type structure [2, 4, 9] and conditions of formation apply to the anions reported here.

The anions of the $La(XW_{11})_2$ type are formed in good yield in the pH range 4–6.5 and are stable over a still wider pH range once they are formed. It is this stability of the $La(XW_{11})_2$ complexes in the strong acidic medium that allows their salts to be converted to the free acid by ion-exchange. This,

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*For convenience we shall abbreviate the formula of heteropolycomplexes omitting the charge and the oxygen atoms. Thus BW_{11}, $La(BW_{11})_2$ refer to $BW_{11}O_{39}^{9-}$ and $La(BW_{11}O_{39})_2^{15-}$ respectively. The complete formulas of the complexes reported here are given in the Table.

TABLE. Analytical Data for La^{3+} Complexes with Heteropoly Ligands.[a]

Salt	K/Cs	La	X/X'	W	Loss on Ignition (%)
$K_{15}[La(BW_{11}O_{39})_2]25H_2O$	9.00 (9.03)	2.11 (2.14)	– (0.333)	62.0 (62.3)	7.10 (6.93)
$Cs_{15}[La(BW_{11}O_{39})_2]12H_2O$	25.9 (26.0)	1.78 (1.81)	– (0.269)	52.6 (52.7)	3.00 (2.82)
$K_{13}[La(SiW_{11}O_{39})_2]25H_2O$	7.76 (7.88)	2.13 (2.15)	– (0.871)	62.6 (62.7)	7.21 (6.98)
$Cs_{13}[La(SiW_{11}O_{39})_2]15H_2O$	23.0 (23.1)	1.86 (1.85)	– (0.750)	53.8 (54.0)	3.50 (3.60)
$K_{13}[La(GeW_{11}O_{39})_2]26H_2O$	7.69 (7.75)	2.15 (2.12)	2.10 (2.21)	61.6 (61.7)	7.32 (7.14)
$Cs_{13}[La(GeW_{11}O_{39})_2]12H_2O$	22.8 (22.9)	1.86 (1.84)	1.96 (1.93)	53.7 (53.8)	3.10 (2.87)
$K_{11}[La(PW_{11}O_{39})_2]30H_2O$	6.63 (6.65)	2.10 (2.14)	0.971 (0.968)	62.3 (62.5)	8.00 (8.35)
$Cs_{11}[La(PW_{11}O_{39})_2]13H_2O$	19.9 (20.3)	1.91 (1.93)	0.870 (0.861)	55.9 (56.2)	3.10 (3.25)
$K_{11}[La(AsW_{11}O_{39})_2]30H_2O$	6.60 (6.56)	2.10 (2.12)	2.25 (2.28)	61.5 (61.7)	7.96 (8.24)
$Cs_{11}[La(AsW_{11}O_{39})_2]12H_2O$	20.3 (20.1)	1.89 (1.91)	2.04 (2.06)	55.3 (55.7)	3.00 (2.97)
$K_{17}[La(P_2W_{17}O_{61})_2]20H_2O$	7.06 (7.00)	1.44 (1.46)	1.28 (1.30)	65.4 (65.8)	3.59 (3.79)
$Cs_{17}[La(P_2W_{17}O_{61})_2]10H_2O$	20.3 (20.7)	1.25 (1.27)	1.10 (1.13)	56.9 (57.3)	1.49 (1.65)
$K_{17}[La(As_2W_{17}O_{61})_2]20H_2O$	6.79 (6.87)	1.45 (1.43)	3.07 (3.10)	64.1 (64.6)	3.63 (3.72)
$Cs_{17}[La(As_2W_{17}O_{61})_2]12H_2O$	19.9 (20.3)	1.25 (1.24)	2.66 (2.69)	56.5 (56.2)	1.80 (1.94)

[a] Calculated values (%) in parentheses.

however, as noted for other complexes of boron [8] does not apply to $La(BW_{11})_2$ which exists in the pH range 3–6.5 after isolation and decomposes in the strong acidic medium necessary for the existence of the free acids. The charges of the $La(XW_{11})_2$ type of complexes were thus also confirmed by conversion into free acids by ion-exchange and titrating potentiometrically. The appearance of a single end-point suggests that the successive pH values are close to one another. The complexes of the type $La(X_2W_{17})_2$ are unstable outside the pH range ~ 3.5–7 and thus their free acids cannot be made.

Base attack on both $La(XW_{11})_2$ and $La(X'_2W_{17})_2$ is imperceptibly slow at room temperature. However, at higher temperatures (80–100 °C) in the presence of excess base $La(XW_{11})_2$ decompose into metal hydroxide, $X^{n+}O_4^{(8-n)-}$ and WO_4^{2-} in a few minutes. Under similar conditions it takes over an hour for the $La(X'_2W_{17})_2$ anions to decompose. Further investigations are needed before a plausible explanation can be offered for the relative inertness of the $La(X'_2W_{17})_2$ towards base attack. The slower reaction and hence the higher activation energy in this case implies that the decomposition proceeds *via* some stable intermediate.

The anions react in solution with transition metal ions or lanthanide ions (Z) by replacing lanthanum in the parent anion with Z. However, these reactions are not quantitative [1, 8].

There are no absorption bands in the visible region, consequently all the complexes described are white in colour. However, like all the other polyions there are intense charge transfer transitions in the ultraviolet region [2].

References

1 T. J. R. Weakley and S. A. Malik, *J. Inorg. Nucl. Chem., 29,* 2935 (1967); S. A. Malik and T. J. R. Weakley, *J. Chem. Soc. A,* 2647 (1968); A. M. Qureshi, S. A. Zubairi and S. A. Malik, *J. Inorg. Nucl. Chem., 38,* 879 (1976).

2 T J. R. Weakley, *Structure and Bonding, 18,* 131 (1974).

3 P. Souchay, "Polyanions and Polycations", Gauthiers–Villars, Paris (1963); "Ions Minéraux Condensés", Masson, Paris (1969).

4 H. T. Evans, Jr., *Perspectives Struct. Chem., 4,* 1 (1971).

5 L. P. Kazanskii, E. A. Torchenkora and V. I. Spitsyn, *Russ. Chem. Rev., 43,* 525 (1974).

6 R. D. Peacock and T. J. R. Weakley, *J. Chem. Soc. A,* 1836 (1971).

7 B. Gruttner and G. Jander, in "Handbook of Preparative Inorganic Chemistry", ed. G. Brauer, Academic Press, New York, 2nd ed., Vol. II, p. 1698–1740 (1965); E. O. North and W Haney, *Inorg. Synth., 1,* 127 (1939); J. C. Builar, *Inorg. Synth., 1,* 132 (1939); F. Kehrmann, *Z. Anorg. Chem., 22,* 285 (1900); H. Wu, *J. Biol. Chem., 43,* 189 (1920); P. Souchay, *Ann. Chim. France, 2, 12,* 203 (1947).

8 C. Tourné and G. Tourné, *Bull. Soc. Chim. Fr.,* 1124 (1969); C. Tourné and G. Tourné, *C. R. Hebd. Seanc. Acad. Sci. Paris, C266,* 702 (1968); C. Tourné, G. Tourné, S. A. Malik and T. J. R. Weakley, *J. Inorg. Nucl. Chem., 32,* 3875 (1970); M. Bauchet, C. Tourné and M. G. Tourné, *C. R. Hebd. Seanc. Acad. Sci. Paris, C275,* 407 (1972).

9 J. F. Keggin, *Nature, 131,* 908 (1933); *Proc. Roy. Soc., A144,* 75 (1934); B. Dawson, *Acta Cryst., 6,* 113 (1953).

10 L. C. W. Baker, V. E. S. Baker, M. T Pope, M. Shibata, O. W. Rollins, J. H Fang and L. L. Koh, *J. Chem. Soc.,* 2329 (1966); L. C. W. Baker, V. E. S. Baker, S. H. Vasafi, G. A. Candela and A. H. Kahn, *J. Chem. Phys., 56,* 4917 (1972); *J. Am. Chem. Soc., 94,* 5499 (1974).

11 T. J R. Weakley, *J. Chem. Soc. Dalton,* 341 (1973). M. T. Pope and R. A. Prados, *J. Am. Chem. Soc., 96,* 6779 (1974); M. T. Pope, S. E. O'Donnel and R. A. Prados, *Chem. Comm.,* 22 (1975).