THE SYNTHESIS AND REACTIVITY OF SOME PEROXO COMPLEXES OF MOLYBDENUM(VI) AND TUNGSTEN(VI)

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(Received 30 June 1992; accepted 13 July 1992)

Abstract—Some new peroxo complexes of molybdenum(VI) and tungsten(VI) containing organic dibasic acids and heterocyclic amines have been prepared and characterized. The complexes have the composition $[M(O)(O_2)(acid) \cdot L]$, where M = molybdenum(VI) or tungsten(VI), acid = dianion of diphenic acid (da) or homophthalic acid (hp) and L = 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen). The complexes did not oxidize allyl alcohol, but oxidized triphenylphosphine and triphenylarsine to their respective oxides.

Studies on peroxo complexes have received considerable attention due to their application in synthetic organic chemistry.¹⁻¹⁰ Peroxo complexes of transition metals are sources of active oxygen atoms and many of these complexes can be used as efficient stoichiometric or catalytic oxidants for inorganic and organic substrates.⁷⁻¹¹ The reactivity of peroxo complexes depends on the nature of the other auxiliary ligands used. Keeping these facts in view, we herein report the synthesis and properties of some new peroxo complexes of molybdenum(VI) and tungsten(VI) containing the diphenate or homophthalate anion and 2,2'-bipyridine or 1,10-phenanthroline.

EXPERIMENTAL

Physical measurements

The IR spectra were recorded on a Pye–Unicam SP3-300 IR spectrophotometer; spectra between 4000 and 600 cm⁻¹ were recorded as KBr pellets and between 600 and 200 cm⁻¹ as Nujol mulls sandwiched between CsI plates. Conductivities of 1.0×10^{-3} mol dm⁻³ solutions of the complexes in dimethylsulphoxide were measured at 27°C using a WPA CM35 conductivity meter and a dip-type cell with platinized electrodes. Decomposition points of the complexes were recorded with an Electrothermal Melting Point Apparatus. The molecular masses of the complexes were determined in nitrobenzene by cryoscopic methods.

Reagents

All chemicals used were of reagent grade. Molybdenum trioxide and tungsten trioxide were obtained from BDH Chemicals Ltd, U.K. Diphenic acid and homophthalic acid were obtained from Fluka Chemicals, Switzerland, and all other chemicals were used as supplied by E. Merck.

Analyses

Molybdenum and tungsten were determined gravimetrically.¹² Carbon, hydrogen and nitrogen analyses were carried out by the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow, India.

Preparation of complexes

General method for the preparation of the complexes (1-8): $[M(O)(O_2)(acid) \cdot L]$ (M = Mo^{VI} or W^{VI}; acid = dianion of diphenic or homophthalic acid; L = 2,2'-bipyridine or 1,10-phenanthroline). A suspension of MO₃ (0.01 mol) in 30% H₂O₂ (100 cm³) was stirred overnight at 50°C. This was filtered and to the filtrate was added a solution of diphenic acid or homophthalic acid (0.01 mol) in methanol (40 cm³), followed by the addition of L (0.01 mol) in methanol (30 cm³). The mixture was stirred while cooling at the same time in an ice-salt bath. The orange-yellow precipitate which appeared was filtered, washed several times successively with water and methanol and dried in a vacuum desiccator over anhydrous silica gel.

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Attempted reactions of the complexes with allyl alcohol

Compound 1 (1.62 g, 0.003 mol) was suspended in THF (30 cm³) and a stoichiometric amount of allyl alcohol was added. The mixture was stirred under reflux at 60°C for 48 h, but failed to produce any reaction product.

Refluxing 4, 5 or 7 with allyl alcohol in a 1:1 molar ratio in THF medium for 48 h also failed to produce any reaction product.

Reactions of 1 and 5 with triphenylphospine (reaction A)

A solution of triphenylphospine (0.786 g, 0.003 mol) in THF (20 cm³) was added to a suspension of compound 1 (1.62 g, 0.003 mol) or compound 5 (1.88 g, 0.003 mol) in THF (40 cm³). The mixture was stirred under reflux for 48 h. TLC indicated that the reaction was complete. The reaction mixture was filtered and the residue collected. A yellowish-white powder was recovered from the filtrate, which was identified by mixed melting point as triphenylphosphine oxide; m.p. 156–157°C.

Reactions of 3 and 8 with triphenylarsine (reaction B)

A solution of triphenylarsine (0.981 g, 0.003 mol) in THF (35 cm³) was added to a suspension of compound **3** (1.43 g, 0.003 mol) or compound **8** (1.77 g, 0.003 mol) in THF (50 cm³). The mixture was refluxed for 60 h. TLC indicated that triphenylarsine was converted completely into triphenylarsine oxide. The reaction mixture was filtered and the residue collected. Evaporation of the filtrate yielded the product, m.p. 187–189°C (lit.¹³ m.p. 190–192°C).

RESULTS AND DISCUSSION

The analytical and physical data of the complexes are presented in Table 1. All the complexes are insoluble in water, but soluble in dimethylsulphoxide and nitrobenzene. The molar conductance values (Table 1) indicate that the complexes are non-electrolytes in dimethylsulphoxide, revealing that the anions are covalently bonded in all the cases. The calculated and experimental values of the molecular masses of the complexes (Table 1) indicate their existence in the monomeric form. The results of elemental analyses, conductance values and molecular masses of the complexes are compatible with their general formula, [M(O)(O₂)(acid) · L].

IR spectral data of the complexes are shown in Table 2. The complexes display v(C=O) bands at 1620–1640 cm⁻¹ and v(C—O) bands at 1400–1425 cm,⁻¹ significantly lower than the values of free diphenic acid (1700 and 1450 cm⁻¹) or homophthalic acid (1700 and 1440 cm^{-1}). This indicates the coordination of diphenic acid (daH₂) or homophthalic acid (hpH₂) through their carboxylate anions. The broad band observed at ca 3500 cm⁻¹ due to the v(O-H) mode of the free daH₂ molecules disappears upon coordination, revealing that diphenic acid or homophthalic acid behaves as a bidentate, dinegative ligand coordinating through both carboxylate anions. Further, the presence of M - O' (O' = oxygen in diphenic or homophthalic acid) bonding is evident from the appearance of v(M-O') modes at 420-450 cm⁻¹ in the spectra of the complexes.¹⁴ The complexes display v(M=0)modes in the region 920–945 cm^{-1} .

The band observed at ~1600 cm⁻¹ due to v(C=N) of free bipyridine and phenanthroline shifted to *ca* 1560 cm⁻¹ in the spectra of the complexes, indicating the coordination of the heterocyclic nitrogen. Again, two metal-sensitive modes of bipyridine and phenanthroline observed at *ca* 740 and *ca* 995 cm⁻¹ undergo shifts to higher frequencies in the present complexes confirming their coordination through nitrogen.¹⁵ Further support for the presence of M—N bonding is apparent from the v(M-N) modes at 335–360 cm⁻¹ in the spectra of the complexes.¹⁶

The metal peroxo grouping gives rise to three IR active vibrational modes. These are mainly O—O stretching (v_1) , the symmetric M—O stretch (v_2) and the antisymmetric M—O stretch (v_3) . The characteristic $v_1(O-O)$ modes of the complexes appear at 820–880 cm⁻¹. It is observed that the v_1 mode decreases upon passing from molybdenum complexes (1-4) to the corresponding tungsten complexes (5-8). The present study thus suggests that for the M(O₂) grouping, the v_1 modes decrease with an increase in the atmoic number of the metal in a particular group. In the present complexes, the v_2 and v_3 modes appear at 590–620 and 650–695 cm⁻¹, respectively.

Reactivity

The present peroxo complexes were found to liberate iodine on treatment with aqueous potassium iodide. Based on this observation, the possible reactivity of the complexes towards olefinic compounds could be explored. The complexes were allowed to react stoichiometrically with allyl alcohol, which failed to produce any reaction. However, the complexes were found to oxidize triphenylphosphine

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			Decomposit	ion				:		
Compc	punc	No.	point (±0.5°C)	Molec	cular Me ss %	tal Carbon 6 %	Hydrogen %	Nitrogen %	Molar con $(\Omega^{-1} \text{ cm}^2)$	fuctance mol ⁻¹)
[Mo(O)(O ₂)(da)([(bpy)]	1	95	52	9 17	.3 53.0	3.1	5.2	6.8	
				(54	0) (17	.7) (53.3)	(3.0)	(5.2)		
[Mo(O)(O ₂)(da)((phen)]	2	128	.09	2 16	.8 55.1	2.8	4.8	3.2	
				(56	4) (17	.0) (55.3)	(2.8)	(2.0)		
[Mo(O)(O ₂)(hp)([(bpy)]	£	110	51	9 19	.6 47.2	2.8	5.6	5.5	_
				(47	8) (20	.1) (47.7)	(2.9)	(5.8)		
[Mo(O)(O ₂)(hp)((phen)]	4	98	48	3 19	.3 50.4	2.9	5.3	2.3	
	•			(50)	2) (19	.1) (50.2)	(2.8)	(2.6)		
$[W(O)(O_2)(da)(b$	[(yqt	'n	103	58	4 28	.9 45.4	2.4	4.3	1.5	
				(62	8) (29	.3) (45.9)	(2.6)	(4.4)		
$[W(O)(O_2)(da)(p)]$	then)]	9	86	.99	5 27	.7 47.4	2.3	4.0	7.6	
	!			(65	2) (28	.2) (47.9)	(2.5)	(4.3)		
[W(O)(O ₂)(hp)(b	[(yqt	7	110	53	6 32	.1 40.0	2.6	4.8	6.3	
				(56	6) (32	.5) (40.3)	(2.5)	(4.9)		
[W(O)(O)(D ₂)(hp)(p	when)]	30	90	62	4 30	.7 42.3	2.2	4.6	4.2	
				(59	0) (31	.1) (42.7)	(2.4)	(4.7)		
$da^{2-} = C_{14}H_8$	$O_4, hp^{2-} = C_9 F$	H_6O_4 , bpy = C	$^{1}_{10}H_8N_2$, phen =	$= C_{12}H_8N_2.$						
				Table	2. IR spectral dat	a (cm ⁻¹)ª				
						(0/m)-"	M) "	6		
Compound	v(C==0)	v(C==N)	v(C0)	v(M==0)	v ₁ (0—0)				((N—N)
-	1630s	1555s	1410m	930s	875s	660m	610m	4	150w	345m
7	1640s	1570s	1400s	925s	860s	650m	595m	Т	t30m	360m
ę	1625s	1550m	1420s	920s	880s	695m	590m	4	145w	340w
4	1620s	1570m	1425s	920s	870s	690m	600w	7	120w	360m
ŝ	1635s	1560s	1420m	925s	840s	685m	620m	4	435m	340w
9	1630s	1580s	1410s	945s	825s	650m	600m	4	420m	355w
٢	1640s	1560s	1420m	925s	820s	665m	610w	P	150w	335w
œ	1630s	1575m	1400m	920s	850s	680m	600m	4	145w	350m

^a Relative band intensities are denoted by s, m and w meaning strong, medium and weak, respectively.

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(reaction A) and triphenylarsine (reaction B) to their respective oxides. The products display IR bands at 1195 and 880 cm⁻¹, due to v(P=O)and v(As=O) modes, respectively.^{13,17,18} The IR spectra of the residue of reactions A and B showed the disappearance of $v_1(O=O)$ bands, which indicates the transfer of the peroxo oxygen to the substrates. A possible reaction path is given in Scheme 1.

Acknowledgement—We are grateful to the Bangladesh University Grants Commission for the award of a Research Fellowship to M.M.U.

REFERENCES

- H. Mimoun, I. S. de Roch and L. Sajus, *Tetrahedron* 1970, 26, 37.
- D. A. Muccigrosso, S. E. Jacobson, P. A. Apgar and F. Mares, J. Am. Chem. Soc. 1978, 100, 7063.
- S. E. Jacobson, D. A. Muccigrosso and F. Mares, J. Org. Chem. 1979, 44, 921.
- G. A. Olah and J. Welch, J. Org. Chem. 1978, 43, 2830.

- T. Katsuki and K. B. Sharpless, J. Am. Chem. Soc. 1980, 102, 5974.
- B. E. Rossiter, T. Katsuki and K. B. Sharpless, J. Am. Chem. Soc. 1981, 103, 464.
- 7. A. D. Westland, F. Haque and J. M. Bouchard, Inorg. Chem. 1980, 19, 2255.
- 8. H. Mimoun, J. Molec. Catal. 1980, 7, 1.
- A. D. Westland and M. T. H. Tarafder, *Inorg. Chem.* 1982, 21, 3228.
- M. T. H. Tarafder and A. R. Khan, *Polyhedron* 1987, 6, 275.
- 11. M. T. H. Tarafder and A. Ahmed, Ind. J. Chem. 1986, 25A, 729.
- 12. A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd edn, pp. 506, 566. Longmans, Green and Co., London (1961).
- 13. J. Bernstein, M. Halmann, S. Pinchas and D. Samuel, J. Chem. Soc. 1964, 821.
- 14. R. D. Hancock and D. A. Thornton, J. Molec. Struct. 1970, 6, 441.
- 15. S. P. Sinha, Spectrochim. Acta 1964, 20, 879.
- B. Hutchinson, J. Takemoto and K. Nakamoto, J. Am. Chem. Soc. 1970, 92, 3335.
- D. M. L. Goodgame and F. A. Cotton, J. Chem. Soc. 1961, 2298.
- D. Brown, J. Hill and C. E. F. Rickard, J. Chem. Soc. 1970, A, 497.