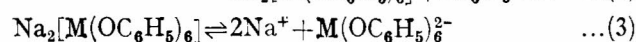
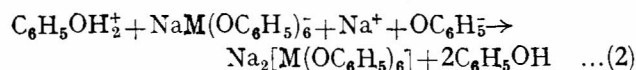
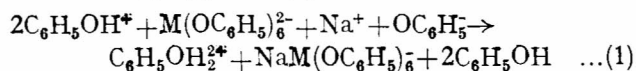


Fig. 1 — Conductometric titrations between acids and bases in phenol at 50°

other tertiary bases with phenol follow a similar pattern (unpublished data).

Strong acceptor molecules such as antimony pentachloride, boron trichloride, aluminium trichloride, etc., readily get solvolyzed in fused phenol at 45°. In the case of tetrachlorides of tin and titanium, partially solvolyzed products of composition $\text{SnCl}_3(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$ and $\text{TiCl}_3(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$ are obtained. Complete solvolysis of these compounds has been carried out to get $\text{Sn}(\text{OC}_6\text{H}_5)_4$ and $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{C}_6\text{H}_5\text{OH}$ respectively (unpublished data). Acid-base titrations of $\text{SnCl}_3(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$ against $\text{C}_6\text{H}_5\text{ONa}$ or $\text{C}_5\text{H}_5\text{N}$ have been carried out. These titrations have been followed both conductometrically and with the help of visual indicators such as malachite green and crystal violet (Fig. 1). There are two breaks in the conductance-composition curves (Fig. 1) suggesting the dibasic character of the acid. Similarly titrations of $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{C}_6\text{H}_5\text{OH}$ against pyridine or sodium phenoxide have also been carried out. Compounds of composition $\text{Na}_2\text{Ti}(\text{OC}_6\text{H}_5)_6$ and $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ have been isolated from the solutions. Compounds of similar nature have already been reported in the case of alkoxydes^{13,14}. The titrations apparently follow reactions (1), (2) and (3).



By analogy with the behaviour of methyl alcohol¹⁵ and acetic acid¹⁶⁻¹⁸ and in the light of above observa-

tions, the possible mode of ionization of phenol may be postulated as



References

- HARROD, J. F. & TAYLOR, K. R., *Inorg. Chem.*, **14** (1975), 1541.
- BIRD, P., FRASAR, A. R. & LAU, C. F., *Inorg. Chem.*, **12** (1973), 1324.
- MALHOTRA, K. C., MAHAJAN, R. K. & CHAUDHRY, S. C., *J. inorg. nucl. Chem.*, (communicated).
- BIRCHALL, T., BOURNS, A. N., GILLESPIE, R. T. & SMITH, P. J., *Can. J. Chem.*, **43** (1964), 1433.
- PARRINGTON, B. D. & CHILD, R. F., *Chem. Commun.*, (1970), 1581.
- BLACKSTOCK, S. M., RICHARD, K. E. & WRIGHT, G. J., *Can. J. Chem.*, **52** (1974), 331.
- MALHOTRA, K. C. & BALI, A. K., *Indian J. Chem.*, **13** (1975), 699.
- GREENWOOD, N. N. & WADE, K., *J. chem. Soc.*, (1958), 1671.
- PAUL, R. C., PAUL, K. K. & MALHOTRA, K. C., *Chemistry Ind. (London)*, (1968), 1227.
- PAUL, R. C. & CHADHA, S. L., *Spectrochim. Acta*, **22** (1966), 615.
- CORDES, A. W. & HUGHES, T. V., *Inorg. Chem.*, **3** (1964), 1640.
- HUNSHUGER, H., *J. Am. chem. Soc.*, **72** (1950), 5626.
- MEHROTRA, R. C. & MEHROTRA, A., *Inorg. Chem.*, **11** (1972), 2170.
- PAUL, R. C., MADAN, H. & CHADHA, S. L., *J. inorg. nucl. Chem.*, **36** (1974), 737.
- LUDMAN, C. J. & WADDINGTON, T. C., *J. chem. Soc.*, (1966), 1816.
- PAUL, R. C., VASISHT, S. K., MALHOTRA, K. C. & PAHIL, S. S., *J. scient. ind. Res.*, **21B** (1962), 552.
- PAUL, R. C., VASISHT, S. K., MALHOTRA, S. K. & PAHIL, S. S., *Anal. Chem.*, **34** (1962), 820.
- PAUL, R. C., KAPOOR, K. R. & PAHIL, S. S., *J. scient. ind. Res.*, **21B** (1962), 533.

Co(II) Complexes of Pyridine-2-aldoxime & 6-Methylpyridine-2-aldoxime

S. K. BHASIN & A. N. BHAT

Department of Chemistry, University of Delhi, Delhi 110007

Received 19 January 1976; accepted 26 April 1976

The reaction in acetone of $\text{CoCl}_2 \cdot \text{H}_2\text{O}$ with pyridine-2-aldoxime (HPOX) and 6-methylpyridine-2-aldoxime (HMePOX) in different stoichiometric ratios (1:2 and 1:3) in the absence and presence of hydrogen peroxide has yielded different Co(II) complexes. One of these, viz. $\text{Co}(\text{HPOX})_2\text{Cl}_2$ is identical with that reported earlier in literature [*Aust. J. Chem.*, **27** (1974), 2475]. The IR studies on these complexes indicate that in some cases, one ligand is ionized and the other unionized whereas in some cases both the ligands in the complexes are unionized. All the complexes are cationic. The measured high magnetic moments rule out +3 oxidation state of the metal ion in any of these complexes.

THE ligands pyridine-2-aldoxime (HPOX) and its 6-methyl derivative (HMePOX) are useful analytical reagents¹⁻⁵. Stability constants of their complexes with trivalent lanthanon ions have been reported⁶ and complexes of HPOX with Ni(II), Pt(II), Pd(II)^{7,9} and Cu(II)^{10,11} have also been

investigated. The Co(II) complex of HPOX was formulated as $\text{Co}(\text{HPOX})_2 \cdot 2\text{H}_2\text{O} \cdot \text{Cl}_2$ (ref. 12) but on reinvestigation was found to be $\text{Co}(\text{HPOX})_2 \cdot \text{Cl}_2$ (ref. 13).

The present communication deals with preparation and characterization of the different Co(II) complexes of HPOX and HMePOX.

HPOX and HMePOX [F. Raschig GmbH (Ludwigshafen)] were used after crystallization from water and ethanol respectively. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and acetone were of AR (BDH) grade. Cobalt was estimated by the standard gravimetric procedure¹⁴.

A strong cation exchange resin 4765 (E. Merck) and anion exchanger IR-45 (OH) (Rohm & Hass) were used.

Magnetic measurements were determined on solid samples using Gouy type balance. $\text{HgCo}(\text{SCN})_4$ was used as the standard.

Preparation of the complexes — Cobalt chloride hexahydrate (0.01 mole) dissolved in boiling acetone (40 ml) was added to a solution containing stoichiometric quantity of the ligand (0.02 mole) in acetone (20 ml). The mixture was refluxed for 2 hr when the red complex precipitated out. It was filtered, washed repeatedly with hot acetone and dried *in vacuo* over P_2O_5 at 110° for 3 hr. The green complexes were obtained from similar mixtures which had been refluxed in the presence of 30% H_2O_2 (15 ml). The following complexes (A to E) were obtained:

(A) $\text{Co}(\text{C}_6\text{H}_6\text{N}_2\text{O})\text{Cl}_2$, red, m.p. 225° (Found: C, 39.5; H, 3.5; N, 14.7; Co, 14.9. Calc.: C, 38.5; H, 3.2; N, 14.9; Co, 15.7%).

(B) $\text{Co}(\text{C}_6\text{H}_5\text{N}_2\text{O})(\text{C}_6\text{H}_6\text{N}_2\text{O})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, green, m.p. 200° (Found: C, 38.8; H, 3.5; N, 14.0; Co, 14.9. Calc.: C, 38.56; H, 3.48; N, 14.9; Co, 15.7%).

(C) $\text{Co}(\text{C}_7\text{H}_8\text{N}_2\text{O})_2 \cdot \text{Cl}_2$, red, m.p. 230° (Found: C, 41.1; H, 4.1; N, 13.7; Co, 13.8. Calc.: C, 41.8; H, 4.0; N, 13.9; Co, 14.1%).

(D) $\text{Co}(\text{C}_7\text{H}_7\text{N}_2\text{O})(\text{C}_7\text{H}_8\text{N}_2\text{O})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, green, m.p. 165° (Found: C, 41.9; H, 4.0; N, 13.5; Co, 13.4. Calc.: C, 41.8; H, 4.7; N, 13.9; Co, 14.6%).

(E) $\text{Co}(\text{C}_7\text{H}_8\text{N}_2\text{O})_3 \cdot \text{Cl}_2 \cdot \text{H}_2\text{O}$, green, m.p. 222° (Found: C, 45.5; H, 4.4; N, 14.9; Co, 10.9. Calc.: C, 45.3; H, 4.6; N, 15.1; Co, 10.6%).

The complexes A, B, C and E also resulted from the reaction mixtures containing three moles of the ligand per mole of the metal ion.

The compounds isolated in the absence of H_2O_2 are red while those obtained in its presence are green in colour. All of them are crystalline, quite stable and sparingly soluble in water (0.002M solutions can be prepared), nitrobenzene and other polar organic solvents, but insoluble in non-polar solvents.

The coloured aqueous solutions of the complexes (0.002M) were passed through the cation exchange resin. The eluant obtained was colourless and contained Cl^- ions in each case thereby indicating that the complex ion involved is a cationic species. The complexes when passed through the anion exchanger gave eluants of the same colour.

Magnetic moments of the complexes were found to be generally high in all the cases. The values were 4.4 (B), 4.6 (C) and 4.2 BM (E). These are

close to the value of 4.65 reported earlier for (A). These values, although high, are within the range of Co(II) complexes having 3 unpaired electrons, and definitely rule out a +3 oxidation state for the metal ion.

The assignment of the bands in the IR spectra* (KBr) of the complexes have been made on the basis of Krause *et al.*⁹ and Holmes *et al.*¹⁵ for the metal chelates of HPOX. On the basis of assignments made earlier for metal-nitrogen ligand complexes^{16,17}, the band at $480\text{--}490\text{ cm}^{-1}$ in the complexes is assigned to $\nu\text{Co-N}$ and the one at $415\text{--}305\text{ cm}^{-1}$ to $\nu\text{N-Co-N}$ (ref. 18). The spectra of the acetylated products of complexes (A) and (C) showed new strong absorption bands at 1740 cm^{-1} ascribable to a free carbonyl group ($-\text{COCH}_3$). No bands were, however, observed for the νOH in the 3000 cm^{-1} region. This is in accordance with the spectra discussed for the acetylated products of Cu(II) and Be(II) with β -resorcyldoximes¹⁹.

The water of crystallization in (B), (D) and (E) was inferred from the bands at $3550\text{--}3400\text{ cm}^{-1}$.

On the basis of the IR studies it has been possible to conclude that while in the case of (A), (C) and (E) the ligands are present in their unionized form, in the case of (B) and (D) one of the ligand moiety is present in the ionized form.

One of us (S.K.B.) thanks the CSIR, New Delhi, for the grant of a senior research fellowship.

References

1. BHAT, A. N. & JAIN, B. D., *J. scient. ind. Res.*, **21B** (1962), 576.
2. GAGLIARDI, E. & PRESINGER, P., *Chem. Abstr.*, **63** (1965), 17132d.
3. PELAUM, A. T., WEHCKING, M. W. & JENSEN, R. E., *Talanta*, **8** (1964), 1193.
4. KUMAR, N., MANKU, G. S., BHAT, A. N. & JAIN, B. D., *Talanta*, **17** (1970), 873.
5. BHAT, A. N. & JAIN, B. D., *Proc. Indian Acad. Sci.*, **56A** (1962), 285.
6. KUMAR, N., MANKU, G. S., BHAT, A. N. & JAIN, B. D., *J. less-common Metals*, **21** (1970), 23.
7. KRAUSE, R. A. & BUSCH, D. N., *Nature*, **181** (1958), 1529.
8. KRAUSE, R. A. & BUSCH, D. N., *J. Am. chem. Soc.*, **82** (1960), 4830.
9. KRAUSE, R. A., COLTHUP, N. B. & BUSCH, D. N., *J. phys. Chem.*, **65** (1961), 2216.
10. LIU, C. N. & LIU, C. F., *J. Am. chem. Soc.*, **23** (1961), 4169.
11. FAUCHERRE, J. & PETITFOUX, C., *Bull. Soc. chim. Fr.*, (1965), 347.
12. BLACKMORE, M. W. & MAGEE, R. J., *Aust. J. Chem.*, **20** (1967), 429.
13. GRANT, M. W. & MAGEE, R. J., *Aust. J. Chem.*, **27** (1974), 2475.
14. VOGEL, A. I., *A text book of quantitative inorganic analysis* (Longmans Green & Co. Ltd, London), 1961, 529.
15. HOLMES, F., LESS, G. & UNDERHILL, A. E., *J. chem. Soc.*, (A) (1971), 999.
16. KATRITZKY, A. R., *Q. Rev.*, **13** (1959), 252.
17. POWELL, D. B. & SHEPPARD, N., *J. chem. Soc.*, (1956), 3108.
18. SHIMANOUCHI, T. & NAKAGAWA, I., *Spectrochim. Acta*, **18** (1962), 89.
19. BHASIN, S. K., UMAPATHY, P. & SEN, D. N., *Indian J. Chem.*, **8** (1970), 744.

*Detailed IR data can be had from the authors on request.