

Note

INFRARED AND THERMAL STUDIES OF OXOZIRCONIUM(IV) COMPLEXES OF 2-ACETYL PYRIDINE *N*-OXIDE

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The metal ion complexes of pyridine *N*-oxides have been the subject of four recent reviews [1–4]. Comparatively little is known about the compounds of oxozirconium(IV) with aromatic amine *N*-oxides [5]. Kidani et al. [6] reported that 2-acetyl pyridine coordinates in a bidentate manner. A related ligand, 2-acetyl pyridine *N*-oxide, can also coordinate either in a monodentate or bidentate form. The ligational behaviour of 2-acetyl pyridine *N*-oxide towards some metal ions has already been reported by West and co-workers [7,8]. In the present communication, the metal complexes formed by 2-acetyl pyridine *N*-oxide (APO) with oxozirconium(IV) salts are reported.

EXPERIMENTAL

Lewis acids were obtained as reported in ref. 9, while the ligand, 2-acetyl pyridine *N*-oxide, was prepared by the previous method reported in ref. 10.

All the complexes were isolated by the following method. The oxozirconium(IV) salt in absolute ethanol and a dehydrating agent (2,2'-dimethoxy propane) were refluxed for ca. $\frac{1}{2}$ h. A warm ethanolic solution of the ligand was added dropwise. Some complexes were precipitated after cooling while others precipitated upon addition of anhydrous diethyl ether. The compounds so formed were filtered, washed with ethanol, then with diethyl ether and dried in vacuo over P_4O_{10} .

All the analyses and physical measurements were performed as reported earlier [9].

RESULTS AND DISCUSSION

Table 1 shows analytical data for the new complexes. All the complexes are non-hygroscopic and stable and can be stored for a long period. The

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TABLE 1

Analytical and partial infrared data (cm^{-1}) of oxozirconium(IV) complexes of 2-acetyl pyridine *N*-oxide

| Compound | Found (calcd.)(%) | | | $\nu(\text{C}=\text{O})$ | $\nu(\text{N}=\text{O})$ | $\nu(\text{Zr}-\text{O})$ |
|---|-------------------|------------------|------------------|--------------------------|--------------------------|---------------------------|
| | Zr | N | Anion | | | |
| APO | — | — | — | 1695s, br | 1260vs | — |
| ZrOCl ₂ ·2APO | 20.29 (20.13) | 6.09 (6.19) | 15.56 (15.70) | 1700s 1690sh | 1205s | 400m |
| ZrOBr ₂ ·2APO | 16.96 (16.82) | 5.08 (5.17) | 29.42 (29.57) | 1692s | 1210s | 390m |
| ZrOI ₂ ·2APO | 14.52 (14.33) | 4.27 (4.40) | 40.16 (40.00) | 1695s 1690sh | 1207s | 380m |
| ZrO(ClO ₄) ₂ ·6APO | 8.12 (8.06) | 7.29 (7.44) | 17.82 (17.64) | 1693s | 1215s | 395m |
| ZrO(NO ₃) ₂ ·2APO | 18.19 (18.01) | 10.92 (11.08) | — | 1700s | 1200s | 405m |
| ZrO(NCS) ₂ ·2APO | 18.41 (18.30) | 11.06 (11.26) | 23.42 (23.34) | 1700sh 1695m | 1205s | 390m |

vs. very strong; s, strong; m, medium; br, broad; sh, shoulder.

complexes are partially soluble in common organic solvents. Due to this partial solubility of these complexes, their geometry in solution could not be measured.

The carbonyl stretching frequency is a strong band at 1695 cm^{-1} in the free ligand which is not shifted appreciably in the complexes, which clearly indicates that the acetyl group does not participate in the coordination compounds. In the spectra of the amine *N*-oxide examined, a very strong absorption at 1260 cm^{-1} was assigned to the NO stretching vibration mode [7,8], which undergoes a significant negative shift on complexation (Table 1). The decrease in the frequency of the NO stretching vibration is attributed to a change in the nature of the nitrogen–oxygen bond as a result of metal–oxygen coordination [1–4]. An absorption of strong intensity at 850 cm^{-1} has been assigned to the NO bending mode [7,8] and, from the tabulated data (Table 1), it is apparent that only a slight shift of this vibration is observed on complexation [11]. Absorptions associated with CH out-of-plane deformation modes are supposed to undergo a slight positive shift due to tightening of the aromatic ring on complexation. A positive shift of ca. 10 cm^{-1} has been observed in this mode of vibration, which is in agreement with the observations of others [11].

The M–O stretching frequencies observed for these complexes appear at similar positions in the spectra to those found for the metal ion complexes of other aromatic amine *N*-oxides [5]. This is supportive of bonding to the metal ion via the N–O function.

The ν_3 (1100 cm^{-1}) and ν_4 modes (625 cm^{-1}) of the ClO₄ group remain

unsplit showing that the perchlorate groups have a T_d symmetry and are ionic in nature [12]. The absence of a ν_3 band of ionic nitrate (D_{3h}) around 1360 cm^{-1} together with the occurrence of bands at 1505 and 1310 cm^{-1} due to the split ν_3 mode in the lower symmetry indicate the covalent nature of the nitrate group [13,14]. The two combination bands ($\nu_1 + \nu_4$) appeared as weak bands at ca. 1750 and 1710 cm^{-1} in the spectra. Application of the Lever separation method [15], the separation being 40 cm^{-1} in this case, suggests a bidentate nature of the nitrate groups. The presence of bands at ca. 1030 (ν_2), 820 (ν_6) and 740 cm^{-1} (ν_3/ν_5) further confirms the bidentate nature of the nitrate groups. In the thiocyanato complex the presence of bands in the region of 2050 (νCN), 845 (νCS) and 480 cm^{-1} (δNCS) is normally associated with the terminal N -bonding thiocyanate group [16].

The Zr–O characteristic band is observed in all the complexes as a weak band in the 980 – 950 cm^{-1} region [5,12]. In the chlorocomplex, $\nu(\text{Zr–Cl})$ occurs at 290 cm^{-1} , while $\nu(\text{Zr–Br})$ and $\nu(\text{Zr–I})$ could not be observed in the spectral range studied.

THERMAL STUDIES

The thermal investigations of the oxozirconium(IV) complexes with aromatic amine N -oxides were reported in great detail by Agarwal and Rastogi [5]. In the present study, chloro, bromo, thiocyanato, nitrate and perchlorato complexes have been selected for thermal studies.

TABLE 2

Thermal decomposition data for ZrO(IV) complexes of 2-acetyl pyridine N -oxide

| Compound | Decomposition temp. ($^{\circ}\text{C}$) | | Decomposition product | TG wt. loss (%) | | DTG temp. ($^{\circ}\text{C}$) and peak |
|--|--|-------|--|-----------------|--------|---|
| | Initial | Final | | Found | Calcd. | |
| $\text{ZrOCl}_2 \cdot 2\text{APO}$ | 202 | 405 | ZrOCl_2 | 62.36 | 60.61 | 300 endo |
| | 440 | 500 | ZrO_2 | 75.06 | 72.78 | 490 exo |
| $\text{ZrOBr}_2 \cdot 2\text{APO}$ | 195 | 400 | ZrOBr_2 | 52.19 | 50.64 | 290 endo |
| | 430 | 495 | ZrO_2 | 79.86 | 77.26 | 480 exo |
| $\text{ZrO}(\text{NCS})_2 \cdot 2\text{APO}$ | 200 | 410 | $\text{ZrO}(\text{NCS})_2$ | 57.16 | 55.13 | 320 endo |
| | 440 | 500 | ZrO_2 | 77.31 | 75.25 | 460 exo |
| $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{APO}$ | 210 | 415 | $\text{ZrO}(\text{NO}_3)_2$ | 56.32 | 54.25 | 300 endo |
| | 445 | 500 | ZrO_2 | 77.16 | 75.64 | 450 exo |
| $\text{ZrO}(\text{ClO}_4)_2 \cdot 6\text{APO}$ | 180 | 360 | $\text{ZrO}(\text{ClO}_4)_2 \cdot 4\text{APO}$ | 25.92 | 24.29 | |
| | 390 | 425 | $\text{ZrO}(\text{ClO}_4)_2$ | 75.16 | 72.87 | 350 exo |
| | 450 | 505 | ZrO_2 | 91.36 | 89.09 | 460 exo |

The results of thermal analyses are given in Table 2. The TG and DTA curves of the complexes of APO indicate that the complexes have no water of crystallization and are non-hygroscopic in nature. The halo and nitrate complexes decompose endothermally while the perchlorate complex decomposes exothermally with explosion and the evolution of smoke. In the case of the perchlorate complex, two ligand molecules are lost at ca. 210°C forming a stable complex with the composition $ZrO(ClO_4)_2 \cdot 4APO$ and then no stable intermediate product is obtained. The other complexes lost both ligand molecules in the temperature range 200–250°C and finally, at ca. 500°C, ZrO_2 is obtained as an end product.

Thus, the thermal stability falls in the following order: $NCS < ClO_4 < Br < Cl < NO_3$.

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REFERENCES

- 1 M. Orchin and P.J. Schmidt, *Coord. Chem. Rev.*, 3 (1968) 345.
- 2 R.G. Garvey, J.H. Nelson and R.O. Ragsdale, *Coord. Chem. Rev.*, 3 (1968) 375.
- 3 N.M. Karayannis, L.L. Pytlewski and C.M. Mikulski, *Coord. Chem. Rev.*, 11 (1973) 93.
- 4 N.M. Karayannis, A.N. Speca, D.E. Chasan and L.L. Pytlewski, *Coord. Chem. Rev.*, 20 (1976) 37.
- 5 R.K. Agarwal and S.C. Rastogi, *Thermochim. Acta*, 87 (1985) 357, and references therein.
- 6 Y. Kidani, M. Noji and H. Koike, *Bull. Chem. Soc. Jpn.*, 48 (1975) 239.
- 7 V.S. Hagley, R.E. Kohrman and D.X. West, *J. Inorg. Nucl. Chem.*, 39 (1977) 1959.
- 8 D.X. West and R.E. Kohrman, *J. Inorg. Nucl. Chem.*, 41 (1979) 1569.
- 9 R.K. Agarwal, M. Srivastava, P.C. Jain, A.K. Srivastava and T.N. Srivastava, *J. Indian Chem. Soc.*, 57 (1980) 374.
- 10 K. Winterfield and W. Zickle, *Arch. Pharm.*, 302 (1969) 900.
- 11 J.V. Quagliano, J. Fujita, G. Franz, D.J. Philips, J.A. Walmsley and S.Y. Tyree, *J. Am. Chem. Soc.*, 83 (1961) 3770.
- 12 S.K. Madan and A.M. Donohue, *J. Inorg. Nucl. Chem.*, 28 (1966) 1303.
- 13 H. Brintzinger and R.E. Hester, *Inorg. Chem.*, 5 (1966) 980.
- 14 R.E. Hester and W.E.L. Grossman, *Inorg. Chem.*, 5 (1966) 1308.
- 15 A.B.P. Lever, E. Mantiovani and B.S. Ramaswamy, *Can. J. Chem.*, 49 (1971) 1957.
- 16 J.L. Burmeister, *Coord. Chem. Rev.*, 1 (1966) 205; 3 (1968) 225.