Nitrobenzene as a Monodentate (O) and Bidentate (O,O') Ligand: Synthesis and Structures of Zn(PhNO2)$_n$(OTeF5)$_2$ (n = 2, 3)

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An X-ray crystallographic study of the first examples of complexes containing co-ordinated nitrobenzene, [Zn(PhNO2)$_2$(OTeF5)$_2$]$_2$ and Zn(PhNO2)$_3$(OTeF5)$_2$, has proven that nitrobenzene can function as a bidentate (O,O') ligand as well as a monodentate (O) ligand.

Organic nitro compounds are notoriously weak bases.[1] Previous structural studies have demonstrated co-ordination by NO2 groups only when the ligand is anionic (*e.g.*, $CH_2NO_2^-$)[2] or when additional anionic metal-binding groups are present in the nitro compound.[3,4] The co-ordination chemistry of neutral nitroparaffins and nitroaromatics has several important potential applications, including the preparation of 'co-ordinatively unsaturated' catalyst precursors (some metal complexes of tetrahydrofuran[5] and acetonitrile,[6] both of which are much stronger donors than nitrobenzene,[1]

$$ZnEt_2 \quad + \quad 2HOTeF_5 \quad \xrightarrow{\text{PhMe}} \quad Zn(PhMe)_x(OTeF_5)_2 \quad + \quad 2C_2H_6$$

$$\downarrow n\ RNO_2$$

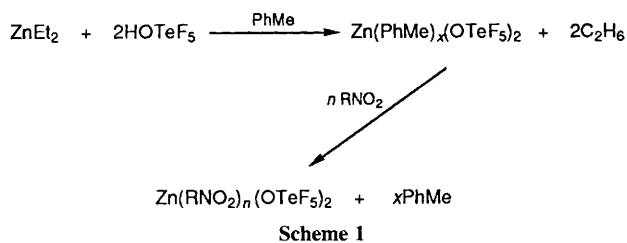$$Zn(RNO_2)_n(OTeF_5)_2 \quad + \quad x\,PhMe$$

Scheme 1

exhibit high catalytic activity), the catalytic transformation of nitroaromatics into ureas and carbamates,[7] and the modification of the stability and burn rate of secondary explosives and propellants (most of which are $C-NO_2$, $O-NO_2$, and $N-NO_2$ compounds).[8]

In this study Zn^{II} complexes of $C-NO_2$ compounds were prepared by treating $Zn(PhMe)_x(OTeF_5)_2$ ($x = 1.5—2.0$)[9] with varying amounts of nitrobenzene or nitromethane (R = Ph or Me) (Scheme 1). These compounds are extremely hygroscopic. More importantly, they rapidly evolve the co-ordinated solvent molecules at 25 °C, making a precise determination of n problematic in most cases. While crystals of $Zn(MeNO_2)_n(OTeF_5)_2$ were stable at low temperature, pseudosymmetry has prevented satisfactory solution and refinement of the structure. Crystals of $[Zn(PhNO_2)_2(OTeF_5)_2]_2$ (1) and $Zn(PhNO_2)_3(OTeF_5)_2$ (2), which were grown from dichloromethane containing two equivalents of nitrobenzene per Zn or from neat nitrobenzene, respectively, gave the structures in Figures 1 and 2.†

The Zn^{II} ions are co-ordinated to two (1) or three (2) nitrobenzene ligands, reflecting the extreme degree of co-ordinative unsaturation in the putative salt $Zn(OTeF_5)_2$.[9] Compound (1) is composed of centrosymmetric dinuclear molecules containing planar Zn_2O_2 cores (Figure 1); each six-co-ordinate Zn^{II} ion is co-ordinated to one monodentate and one bidentate nitrobenzene ligand. Compound (2) is composed of mononuclear complexes: each five-co-ordinate Zn^{II} ion exhibits an approximately trigonal bipyramidal co-ordination geometry and is co-ordinated to three monodentate nitrobenzene ligands. The equatorial $Zn-O(3)$ distance is slightly shorter than the apical $Zn-O(5)$ and $Zn-O(7)$ distances. It is surprising that, with such weak donors, the Zn^{II} ions in (2) are only five-co-ordinate.[10]

All the nitrobenzene ligands in the two structures nearly preserve the planar structure of gaseous[11] and solid[12] nitrobenzene. The Zn^{II} ions are not located in the NO_2 planes of the monodentate nitrobenzene ligands. However, Zn^{II} is only 0.07 Å out of the plane of the bidentate NO_2 group in (1), a degree of planarity shared by Zn^{II} carboxylates containing bidentate CO_2Zn moieties.[13]

The most significant aspect of the structures, however, is the effect of co-ordination on the NO_2 groups. For the monoden-
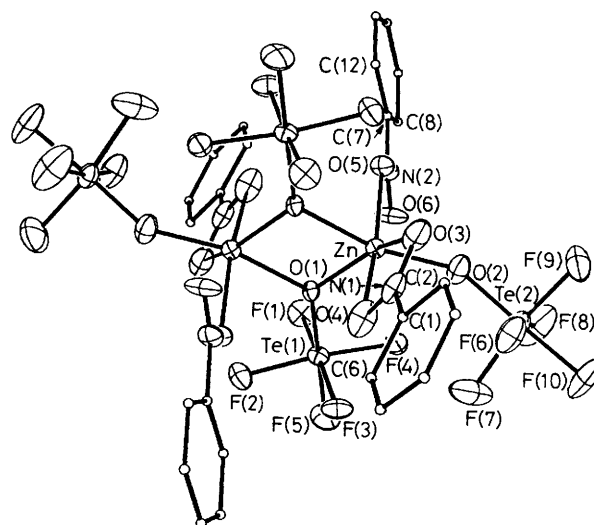
Figure 1. The structure of $[Zn(PhNO_2)_2(OTeF_5)_2]_2$ (1) (50% probability ellipsoids except for carbon atoms; hydrogen atoms omitted for clarity). Selected distances (Å) and angles (°) are: Zn–O(1), 2.012(5); Zn–O(1'), 2.116(6); Zn–O(2), 1.928(7); Zn–O(3), 2.445(6); Zn–O(4), 2.278(5); Zn–O(5), 2.105(4); N(1)–O(3), 1.220(9); N(1)–O(4), 1.26(1); N(2)–O(5), 1.242(8); N(2)–O(6), 1.197(9); N(1)–C(1), 1.435(7); N(2)–C(7), 1.480(7); O(1)–Zn–O(1'), 79.3(2); O(3)–Zn–O(4), 53.5(2); O(4)–Zn–O(5), 159.4(3); O(1)–Zn–O(2), 117.2(3); O(1')–Zn–O(2), 163.4(2); O(3)–N(1)–O(4), 118.9(6); O(5)–N(2)–O(6), 123.5(5); N(1)–O(3)–Zn, 90.2(5); N(1)–O(4)–Zn, 97.3(4); N(2)–O(5)–Zn, 117.2(4).
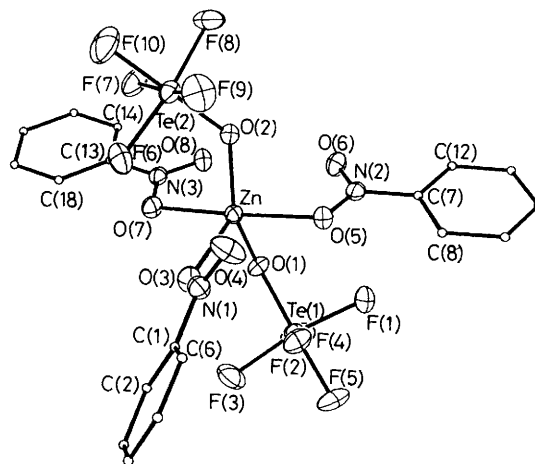

Figure 2. The structure of $Zn(PhNO_2)_3(OTeF_5)_2$ (2) (50% probability ellipsoids except for carbon atoms; hydrogen atoms omitted for clarity). Selected distances (Å) and angles (°) are: Zn–O(1), 1.951(2); Zn–O(2), 1.939(2); Zn–O(3), 2.076(2); Zn–O(5), 2.220(2); Zn–O(7), 2.199(2); Zn⋯O(6), 2.793(2); Zn⋯O(8), 2.850(2); N(1)–O(3), 1.240(4); N(1)–O(4), 1.215(4); N(2)–O(5), 1.243(4); N(2)–O(6), 1.225(3); N(3)–O(7), 1.247(3); N(3)–O(8), 1.222(4); N(1)–C(1), 1.462(4); N(2)–C(7), 1.450(4); N(3)–C(13), 1.454(4); O(1)–Zn–O(2), 149.8(1); O(1)–Zn–O(3), 94.2(1); O(2)–Zn–O(3), 116.0(1); O(5)–Zn–O(7), 176.8(1); O(3)–N(1)–O(4), 122.2(3); O(5)–N(2)–O(6), 121.8(2); O(7)–Zn–O(8), 122.1(2); N(1)–O(3)–Zn, 119.9(2); N(2)–O(5)–Zn, 107.9(2); N(3)–O(7)–Zn, 110.0(2).

tate nitrobenzene ligands, the N–O bond distances involving the bound O atoms are all longer than 1.240(4) Å [N(1)–O(3) in (2)]. For comparison, the N–O bond distance in free nitrobenzene is 1.21(1) Å in the solid state at −30 °C[12] and 1.226 Å in the gas phase.[14]‡ The nitrobenzene ligand in (1) that is co-ordinated to Zn^{II} in asymmetric bidentate fashion also contains an elongated N–O bond. Commensurate with the lengthening (and presumed weakening) of some of the N–O bonds in the co-ordinated nitrobenzene molecules is a shortening (and presumed strengthening) of the C–N bonds [the C–N distances observed in solid and gaseous nitrobenzene are 1.49(2) and 1.492(2) Å, respectively].

IR spectra of (1) and (2) exhibit ν(NO) bands that are shifted with respect to free nitrobenzene. For nitrobenzene dispersed in Nujol, $\nu(NO)_{asym.}$ is 1529 cm^{-1} and $\nu(NO)_{sym.}$ is 1346 cm^{-1}. Compound (1) exhibited ν(NO) bands at 1525, 1503, 1337, and 1328 cm^{-1}. Compound (2) exhibited ν(NO) bands at 1528, 1510, 1340, and 1329 cm^{-1}. The ν(NO) data suggest that both N–O bonds in a monodentate nitrobenzene ligand as well as in a bidentate nitrobenzene ligand are weakened upon co-ordination.

‡ The gas-phase bond distance is quoted, without an estimated standard deviation, in ref. 14.

References

1 V. Gutmann, *Coord. Chem. Rev.*, 1976, **18**, 225; 1967, **2**, 239; 'Coordination Chemistry in Nonaqueous Solvents,' Springer Verlag, Wien–New York, 1969.

2 B. N. Diel and H. Hope, *Inorg. Chem.*, 1986, **25**, 4448, and references therein.

3 S. F. Palopoli, S. J. Geib, A. L. Reingold, and T. B. Brill, *Inorg. Chem.*, 1988, **27**, 2963, and references therein; J. Vincente, M. T. Chicote, J. Martin, M. Artigao, X. Solans, M. Font-Altaba, and M. Aguilo, *J. Chem. Soc., Dalton Trans.*, 1988, 141, and references therein; Y. A. Simonov, V. K. Bel'Skii, G. S. Matuzenko, and N. V. Berbeleu, *Sov. Phys. Crystallogr.*, 1984, **29**, 47, and references therein.

4 Two exceptions involving weak monodentate co-ordination of nitromethane to Cu^{II} and Ti^{IV} are, respectively: B. Duffin and S. C. Wallwork, *Acta Crystallogr.*, 1966, **20**, 210; M. Boyer, Y. Jeannin, C. Rocchiccioli-Deltcheff, and R. Thouvenot, *J. Coord. Chem.*, 1978, **7**, 219.

5 R. F. Jordan and D. F. Taylor, *J. Am. Chem. Soc.*, 1989, **111**, 778.

6 A. Sen, *Adv. Polym. Sci.*, 1986, **73/74**, 125.

7 G. D. Williams, R. R. Whittle, G. L. Geoffroy, and A. L. Reingold, *J. Am. Chem. Soc.*, 1987, **109**, 3936; S. Cenini, *Aspects Homogeneous Catal.*, 1988, **6**, 97.

8 S. F. Palopoli and T. B. Brill, *Inorg. Chem.*, 1988, **27**, 2971, and references therein.

9 P. J. Kellett, Ph.D. Dissertation, Colorado State University, 1989; P. K. Hurlburt, P. J. Kellett, O. P. Anderson, and S. H. Strauss, manuscript in preparation.

10 T. P. E. Auf der Heyde and L. R. Nassimbeni, *Acta Crystallogr., Sect. B*, 1984, **40**, 582.

11 J. H. Høg, L. Nygaard, and G. O. Sørensen, *J. Mol. Struct.*, 1970, **7**, 111.

12 J. Trotter, *Acta Crystallogr.*, 1959, **12**, 884.

13 C. J. Carrell, H. L. Carrell, J. Erlebacher, and J. P. Glusker, *J. Am. Chem. Soc.*, 1988, **110**, 8651.

14 N. I. Sadova and L. V. Vilkov, *Russ. Chem. Rev.*, 1982, **51**, 87.