Inorganica Chimica Acta, *168* (1990) 141–143

Inorganica Chimica Acta
LETTER

Generation of the $Fe(NO)_2^+$ Moiety from $[Fe(H_2O)_6]^{2+}$: Synthesis, Characterisation and Electrochemistry of $[Fe(NO)_2L]_2$ (LH = Benzyl Mercaptan or 2-Mercaptoethanol) and $[Fe(NO)_2$-L–L] (L–LH = 2-Aminobenzene thiol)

R. G. BHATTACHARYYA*, M. MALLIK and P. N. GHOSH

Department of Chemistry, Jadavpur University, Calcutta 700032 (India)

(Received August 18, 1989)

Metal nitrosyls have been reported to possess catalytic properties in organic synthesis [1, 2] and related reactions [3], but these properties have not yet been utilised properly. Formally Fe(–I) complexes (NO^+ formalism) containing the $Fe(NO)_2^+$ moiety known until now are four-coordinate, but prefer a binuclear composition, $[Fe(NO)_2L]_2$ (L = Cl, Br, I [4, 5], C_2H_5S [6]) in the systems isolated, where L atoms bridge two Fe atoms, which in turn interact substantially with each other; the molecules exhibit diamagnetism. These are essentially the familiar Roussin's red ethyl ester and its analogue. We have used a new synthetic route under aqueous and aerobic conditions, and report two new members in the above Roussin's series with L = BM (1; benzyl mercapto anion) and ME (2; 2-mercaptoethanolate anion); we also report herein that a potentially bidentate ligand ABTH (2-aminobenzene thiol) forms a mononuclear species, $[Fe(NO)_2(ABT)]$ (3). This is the first time that such a species (i.e. mononuclear) has been obtained directly from $[Fe(H_2O)_6]^{2+}$ under aqueous and aerobic conditions. Previous reports of a few other monomeric chelates [7–9] have used $Fe(NO)_2^+$ as starting material ($[Fe(NO)_2Br]_2$) in an essentially organic reaction medium.

Experimental

Preparation of $[Fe(NO)_2(BM)]_2$ *(1)*

$FeSO_4·7H_2O$ (5 g; 0.018 mol) was dissolved in 50 cm^3 of 4 M H_2SO_4 and to this solution were added $NaNO_2$ (2 g; 0.023 mol) and benzylmercaptan (5 cm^3; 0.042 mol) simultaneously, with stirring. Stirring was continued for 10 min and the pH of the solution was adjusted to *c.* 6 using 4 M NaOH. A greenish yellow precipitate was obtained which was filtered off, washed with water, isopropanol and light petroleum (60–80 °C) and vacuum dried. The crude product was then extracted in dry benzene and the benzene solution was evaporated to dryness. The yellow solid was further purified by crystallisation from an acetone–water mixture under dinitrogen; yield 1.93 g (44.9%). *Anal.* Calc. for $[Fe(NO)_2(C_6H_5CH_2S)]_2$: C, 35.17; H, 2.95; N, 11.70; S, 13.41; Fe, 23.36. Found: C, 35.1; H, 3.1; N, 11.5; S, 13.2; Fe, 23.0%. MW: calc., 478.1; found, 456. ν(NO) (IR): 1790(s) and 1750(s) cm^{-1}, λ_{max} (electronic): 442 (280) and 762 (20) nm.

Preparation of $[Fe(NO)_2(ME)]_2$ *(2)*

$FeSO_4·7H_2O$ (5 g; 0.018 mol) was dissolved in 50 cm^3 of 4 M H_2SO_4. To this solution, $NaNO_2$ (2 g; 0.029 mol) and 2-mercaptoethanol (5 cm^3; 0.071 mol) were added simultaneously and stirred for 10 min. A dark red solution was thus obtained which was kept at 5 °C for 2 to 3 days. Dark red shiny microcrystals were separated, which were filtered off and washed with water and then dried in a vacuum. Attempted crystallisation destroyed the shiny crystalline nature already obtained and so the original crystals were used directly; yield, 1.39 g (40.1%). *Anal.* Calc. for $[Fe(NO)_2(SCH_2CH_2OH)]_2$: C, 12.45; H, 2.61; N, 14.51; S, 16.61; Fe, 28.94. Found: C, 12.6; H, 2.6; N, 14.4; S, 16.4; Fe, 28.7%. MW: calc. 385.9; found, 360. ν(NO) (IR): 1805(s), 1740(s) cm^{-1}. λ_{max} (electronic): 442 (420) and 762 (25) nm.

Preparation of $[Fe(NO)_2(ABT)]$ *(3)*

The same method as described above was followed using 5 cm^3 of 2-aminobenzene thiol. A black precipitate was obtained, which was filtered off, washed with water, isopropanol and light petroleum (60–80 °C) and vacuum dried. The solid was extracted in dry CH_2Cl_2 and the extract was evaporated to dryness. The solid was then crystallised from an acetone–water mixture in a dinitrogen atmosphere; yield, 2.16 g (50.0%). *Anal.* Calc. for $[Fe(NO)_2(NH_2C_6H_4S)]$: C, 30.02; H, 2.52; N, 17.50; S, 13.35; Fe, 23.26. Found: C, 30.2; H, 2.5; N, 17.2; S, 13.2; Fe, 22.8%. MW: calc., 240.0; found, 238. ν(NO) (IR): 1800(s), 1740(s) cm^{-1}. λ_{max} (electronic): 450 (260), 525 (220), 619 (240) and 788 (90) nm.

Measurements

IR spectra were recorded on a Perkin-Elmer 597 spectrophotometer using KBr discs. Electronic

---

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

spectra were measured using a Hitachi U-3400 UV–Vis–NIR spectrophotometer. A Knauer vapour pressure osmometer (Berlin) was used for molecular weight determinations, calibrating the instrument with benzyl solution and using dichloromethane as solvent. The X-band EPR spectra were recorded with a Varian B 109C spectrometer filled with a quartz dewar for measurement at 77 K. The spectra were calibrated with the help of diphenyl picryl hydrazyl ($g = 2.0037$). Voltammetric measurements were made using a PAR Model 370-4 electrochemistry system [Model 174A polarographic analyser, Model 175 universal programmer, Model RE 0089 XY recorder, Model 173 potentiostat, and Model 179 digital coulometer]. All experiments were performed under a dinitrogen atmosphere unless otherwise mentioned, in a three-electrode cell using a stout platinum wire as the working electrode, a platinum foil as the auxiliary electrode, and a saturated Calomel reference electrode (SCE). All results were collected at 298 K and the reported potentials are uncorrected for junction contribution. Elemental analyses were made on a Perkin-Elmer Model 240C elemental analyser.

Results and Discussion

Apparently, it may seem that since ABT^- is a bidentate ligand it affords a mononuclear complex instead of a binuclear one when unidentate ligands (viz, BM^- and ME^- (this work) or I^- and C_2H_5S [5, 6]) are employed. But, it should be noted that the otherwise potential and versatile bidentate ligand 8-quinolinol does not afford any pure isolable product, and dtc^- (diethyldithiocarbamate anion) and 2-mercapto quinolinate (MQ^-) produce only $[Fe(NO)(dtc)_2]$ and $[Fe(NO)(MQ)_2]$ [10] respectively under the same experimental conditions. So, at present **3** is one of the very few compounds known which contains the mononuclear $Fe(NO)_2^+$ moiety. It is worth noting that isolation of this type of complex was once stated to be a remote possibility [11].

Compounds **1** and **2** are diamagnetic, indicating pronounced Fe–Fe interaction, while **3** (the mononuclear species) is paramagnetic ($\mu_{eff} = 1.9$ BM) and EPR sensitive (a surprisingly axially symmetrical spectrum; $\langle g\rangle_\perp = 2.04$, $\langle g\rangle_\parallel = 2.02$, $\langle g\rangle_{av} = 2.03$; see Fig. 1). The two $\nu(NO)$ vibrations in the IR spectra due to a *cis*-$(NO)_2$ group in compounds **1** to **3** appear in almost identical regions (see Experimental), implying an apparent immunity of these vibrations towards the nuclearity of the complex

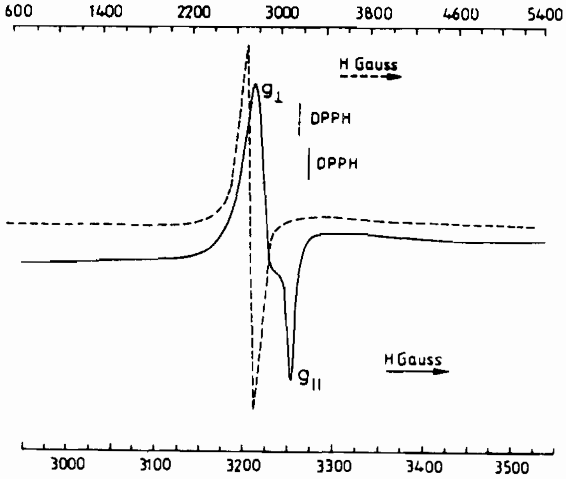

Fig. 1. ESR spectrum of $[Fe(NO)_2(ABT)]$ at 298 K: (——) microcrystalline; (– – –) fluid CH_2Cl_2.

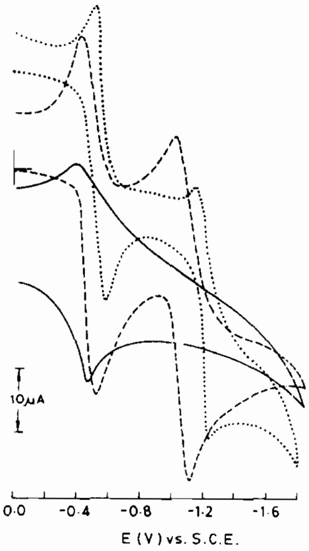

Fig. 2. Cyclic voltammograms of **1** to **3** in CH_3CN at a scan rate of 50 mV s^{-1}.

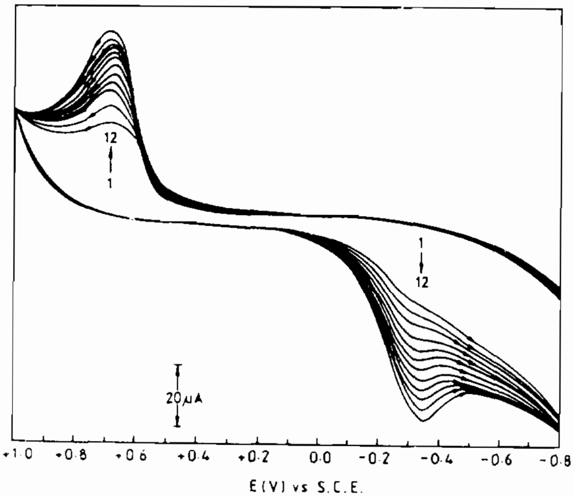

Fig. 3. Typical electropolymerisation of $[Fe(NO)_2(ABT)]$ in CH_3CN in an aerobic medium.

molecules. The M–M interaction in **1** and **2** is perhaps compensated by an enhanced π-acidity of the ABT ligand. The axial symmetry in **3** is again apparent from the observation of four electronic spectral bands (Experimental) assigned to $b_1 \rightarrow b_2$, $b_1 \rightarrow a_1$, $b_1 \rightarrow a_2$ and $b_1 \rightarrow b_1$ in order of increasing energy, for the coordination sphere, compatible with a square-planar (four bands are closely spaced) C_{2v} structure (obviously idealised in the present case and not the strict one) [12]. The Roussin's analogues **1** and **2**, however, show only two such bands positionally corresponding to that of the first and the last of **3**.

The mononuclearity of **3** as against the binuclearity of **1** and **2** is beautifully demonstrated by their cyclic voltammograms (CH_3CN, Pt, tetraethyl ammonium perchlorate). Under a dinitrogen atmosphere, **1** and **2** exhibit two successive and reversible one-electron reductive cyclic responses, corresponding to the existence of the redox couple

$$Fe(NO)_2{}^+ + e^- \rightleftharpoons Fe(NO)_2{}^0$$

implying a stepwise reduction of two metal centres in **1** and **2** (NO^+ or organic ligands do not have any electroactivity in this region). $E^0{}_{298}$ is *c.* 0.50 and -1.2 V versus SCE, as against one such reversible cyclic response at -0.45 V versus SCE in the case of **3** (Fig. 2). Interestingly, in an aerobic medium the CV curve of **3** is typical of an electropolymerisation process [13] (Fig. 3) leading to the deposition of a conducting polymer (in so far as both cathodic and anodic current increase with an increase in deposition) on the working Pt electrode as thin but sturdy layers.

Acknowledgements

Our grateful thanks are due to the UGC, New Delhi, for financial assistance including a Research Fellowship to M.M. We thank Professor A. Chakravorty (IACS, Calcutta) for the ESR spectrum and the Alexander von Humboldt Foundation for the donation of the IR spectrophotometer used in this work.

References

1 E. A. Zuech, W. B. Hughes, D. H. Kubicek and E. T. Kittleman, *J. Am. Chem. Soc., 92* (1970) 528, 532.
2 M. T. Beck, A. Katho' and L. Do'zsa, *Inorg. Chim. Acta, 55* (1981) L55.
3 K. K. Pandey, *Coord. Chem. Rev., 51* (1983) 69.
4 W. Hieber and R. Nast, *Z. Anorg. Allg. Chem., 244* (1940) 23.
5 L. F. Dahl, E. R. de Gil and R. D. Feltham, *J. Am. Chem. Soc., 91* (1969) 1653.
6 J. T. Thomas, J. H. Robertson and E. G. Cox, *Acta Crystallogr., 11* (1958) 599.
7 W. Hieber and H. Fuhrling, *Z. Anorg. Allg. Chem., 377* (1970) 29.
8 W. Hieber and H. Fuhrling, *Z. Anorg. Allg. Chem., 381* (1971) 235.
9 W. Hieber and K. Kaiser, *Z. Anorg. Allg. Chem., 358* (1968) 271.
10 R. G. Bhattacharyya and M. Mallik, unpublished work.
11 C. C. McDonald, W. D. Phillips and H. F. Mower, *J. Am. Chem. Soc., 87* (1965) 3319.
12 J. H. Enermark and R. D. Feltham, *Coord. Chem. Rev., 13* (1974) 339.
13 J. Guay, M. Leclerc and Lê H. Dao, *J. Electroanal. Chem., 251* (1988) 31.