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Structural and X-ray Photoelectron Spectroscopic Properties of Hydrophobic Cobalt(III) 'Cage' Complexes with Dithiocarbamate Anions

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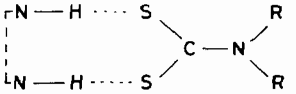
Abstract

The X-ray photoelectron spectra of the hydrophobic encapsulated cobalt(III) complexes, [Co(diNOsar)]$[S_2CNR_2]_3$, are reported, together with a single crystal X-ray structure determination of [Co(diNOsar)]$[S_2CN(CH_2)_4]_3$ (diNOsar = 1,8-dinitro-3,6,9,13,16,19-hexaazabicyclo[6.6.6.]icosane; S_2CNR_2 = *N,N*-dialkyldithiocarbamate). Results show that the Co $2p_{3/2}$ binding energy (*BE*) for the complex cation of 780.5 eV is not significantly different to the *BE* found for $[Co(en)_3]Cl_3$ but is *ca.* 1.4 eV greater than the values recorded for $Co(S_2CNR_2)_3$ complexes. Similarly, S 2p *BE* values are relatively constant for each anion (range 160.8–161.3 eV), but less than the values of 161.9–162.2 eV recorded for $Co(S_2CNR_2)_3$. Crystals of [Co(diNOsar)]$[S_2CN(CH_2)_4]_3$ are monoclinic, space group $C2/c$ with $a = 34.526(7)$, $b = 11.071(2)$, $c = 23.445(3)$ Å and $\beta = 96.37(1)°$. The structure refined to a final R value of 0.065 for 2754 observed ($I > 2.5\sigma(I)$) reflections. Strong hydrogen bonds exist between the sulfur atoms of the dithiocarbamate anion and the secondary amine protons of the complex cation which is stabilized in a C_3lel_3 conformation by these interactions.

Introduction

In earlier work, we have shown that it is possible to synthesize dithiocarbamate (dtc) salts of encapsulated cobalt(III) complexes in which the ionic integrity of the anion is maintained [1, 2]. Interaction between the anion and cation is via symmetrical pairs of strong hydrogen bonds between the secondary amine protons on the cation and the sulfur atoms of the anion.



These complexes present the hydrophobic alkyl groups of the dtc ligand to the solvent rather than the hydrophilic amine hydrogen atoms and, unlike most cobalt(III) cage complexes, are soluble in solvents such as chloroform and toluene rather than water.

We considered that the properties of these complex salts provided a useful opportunity to measure spectroscopic parameters of both the cobalt(III) cations and dithiocarbamate anions in a unique environment and in this paper we report the results of a systematic study of the X-ray photoelectron spectra of the 1:3 salts of the cobalt(III) complex cation (1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6.]icosane)cobalt(III), $[Co(diNOsar)]^{3+}$, with tetramethylene, diethyl and di-isopropyl dithiocarbamate anions, together with a comparative study of the analogous sodium salts and cobalt complexes. To ensure the structures of these cation–anion complexes were similar to the previously reported [Co(AMMEsar)]$[S_2CNEt_2]_3$ complex [1], we also determined, and record here, the crystal structure of the complex, [Co(diNOsar)]$[S_2CN(CH_2)_4]_3$.

Experimental

Preparation of Compounds

The salts [Co(diNOsar)]$[S_2CN(CH_2)_4]_3$ (1), [Co(diNOsar)]$[S_2CNEt_2]_3$ (2) and [Co(diNOsar)]$[S_2CN(i\text{-}Pr)_2]_3$ (3) were prepared as crystalline solids by the slow addition of an aqueous solution of 0.02 mol of the appropriate sodium dithiocarbamate salt in 150 ml of water to a stirred solution of 2.2 g (0.005 mol) of [Co(diNOsar)]Cl_3, also in 150 ml

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of water. The precipitated salt was collected on a Buchner funnel and washed with several 50 ml portions of deionized water. Crystals of **1** suitable for X-ray diffraction studies were grown by the slow evaporation of acetone–water solutions of the compound.

Anal. [Co(diNOsar)] $[S_2CN(CH_2)_4]_3$, melting point (m.p.) dec > 185 °C. Calc for $C_{29}H_{54}CoN_{11}O_4S_6$: C, 39.9; H, 6.24; N, 17.7; S, 22.0. Found: C, 39.5; H, 6.21; N, 17.5; S, 20.2%.

[Co(diNOsar)] $[S_2CNEt_2]_3$, m.p. dec > 170 °C. Calc. for $C_{29}H_{60}CoN_{11}O_4S_6$: C, 39.7; H, 6.88; N, 17.5; S, 21.9. Found: C, 39.2; H, 6.9; N, 17.4; S, 22.1%.

[Co(diNOsar)] $[S_2CN(i\text{-}Pr)_2]_3$, m.p. dec > 175 °C. Calc. for $C_{35}H_{72}CoN_{11}O_4S_6$: C, 43.7; H, 7.54; N, 16.0; S, 20.0. Found: C, 42.3; H, 7.46; N, 15.6; S, 19.0%.

The compound, [Co(diNOsar)]Cl_3 (**4**) was prepared according to standard procedures [3], as were the compounds: hydrated $Na[S_2CN(CH_2)_4]$ (**5**), $Na[S_2CNEt_2]$ (**6**) and $Na[S_2CN(i\text{-}Pr)_2]$ (**7**), $Co(S_2CN(CH_2)_4)_3$ (**8**), $Co(S_2CNEt_2)_3$ (**9**) and $Co(S_2CN(i\text{-}Pr)_2)_3$ (**10**) [4].

Spectroscopy

X-ray photoelectron spectroscopic data were recorded on a PHI 560 system with a base pressure of 5×10^{-10} Torr in the sample chamber. Five minutes after sample introduction the system pressure was *ca.* 10^{-8} Torr as a result of sample outgassing. This improved with extended pumping. Fresh and clean surfaces of complexes **1**–**10** were prepared by grinding the powdered specimens and then attaching the powder to 3M copper backed adhesive tape. The Al Kα line (1486.6 eV) at a source power of 300 W was used. Survey scans were obtained over the binding energy range of 0–1000 eV, in steps of 0.5 eV, and with a constant analyser energy (CAE) of 100 eV. Detailed scans were carried out over all the relevant XPS peaks in steps of 0.2 eV and with a CAE of 25 eV. Signal to noise ratios were improved by repetitive scanning over the regions. Static charging shifts in the peak positions of 2–3 eV were found to occur and the C 1s peaks were used as an internal energy marker. It is likely for these compounds that the dominant contribution to the C 1s peak comes from alkyl carbons with an assumed binding energy of 284.8 eV [5]. For the sodium salts, **5**–**7**, this charge correction resulted in Na 1s *BE* values of 1071.0–1071.2 eV (lit. 1070.9–1071.1 eV [5]). The data were smoothed with a 7th order polynomial fitting routine, but were not processed in any other manner. Binding energy data is tabulated in Table 1.

Structure Determination

The structure of **1** was solved by direct methods. The structure exhibited extensive disorder, both in the complex cation and in the molecules of solvation. Minor sites were located and refined for all six nitrogen atoms coordinated to the cobalt atom and the three methylene carbon atoms of one cap. A complementary occupancy factor was refined for the two sites of these atoms and converged at 0.67:0.33. Numerous partially occupied sites were located for the solvent molecules. These were refined with a group temperature factor and variable occupancies. Partially occupied sites were modelled isotropically. All other non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at calculated sites (C–H, 0.97 Å) with group isotropic thermal parameters. Block-matrix least-squares refinement converged with all shifts less than 0.1σ. The final *R* value is slightly high as a consequence of the disorder found in the structure.

Lattice parameters were determined by a least-squares fit to the setting angles of 25 independent reflections. Data were collected at 294 K in ω–0.33θ scan mode on a Enraf-Nonius CAD4-F four-circle diffractometer, employing graphite monochromated Mo Kα radiation (λ = 0.7106(9) Å). Positional parameters are listed in Table 2 and relevant bond lengths and angles in Table 3.

TABLE 1. XPS Binding Energies (eV) for Compounds **1**–**10**

Compound	Co $2p_{3/2}$	Na 1s	S 2p	N 1s	N 1s(NO_2)
1	780.5		160.8	399.2	405.3
2	780.4		160.9	399.3	405.1
3	780.6		161.0	399.5	405.4
4	780.5			399.8	405.7
5		1071.0	161.0	399.4	
6		1071.2	161.1	399.8	
7		1071.2	161.3	399.5	
8	779.1		162.1	399.5	
9	779.1		161.9	399.5	
10	779.3		162.2	399.5	

TABLE 2. Positional Parameters for [Co(diNOsar)]$[S_2CN(CH_4)_2]_3$ (1)[a]

	x	*y*	*z*	B_{eq}
Cations				
Co	0.1318(1)	0.7289(1)	0.2321(1)	3.25
N(3)	0.1217(3)	0.5994(9)	0.1760(4)	3.91
N(6)	0.1444(3)	0.8292(9)	0.1675(4)	4.11
N(10)	0.1493(3)	0.8588(10)	0.2869(4)	4.37
N(13)	0.1857(3)	0.6667(10)	0.2504(5)	4.24
N(16)	0.1132(3)	0.6211(9)	0.2910(4)	3.85
N(19)	0.0784(3)	0.7890(10)	0.2236(5)	4.81
N(3′)	1.1522(5)	0.6252(15)	0.1742(7)	2.42
N(6′)	1.0973(6)	0.7958(17)	0.1663(8)	3.39
N(10′)	1.1697(6)	0.8665(19)	0.2248(9)	4.13
N(13′)	1.1720(6)	0.6679(18)	0.2920(9)	3.69
N(16′)	1.0970(6)	0.5993(17)	0.2484(9)	3.05
N(19′)	1.1041(5)	0.8283(18)	0.2843(8)	3.58
O(11)	0.1582(2)	0.2823(6)	0.3008(3)	7.55
O(12)	0.1890(3)	0.2937(6)	0.2270(4)	8.20
N(1)	0.1673(3)	0.3358(7)	0.2594(4)	5.00
C(1)	0.1543(2)	0.4658(7)	0.2503(4)	3.78
C(2)	0.1450(3)	0.4842(8)	0.1859(4)	5.36
C(4)	0.1304(3)	0.6449(8)	0.1175(3)	4.40
C(5)	0.1212(3)	0.7761(8)	0.1137(4)	4.57
C(7)	0.1374(4)	0.9602(13)	0.1702(7)	4.59
C(8)	0.1102(3)	0.9917(8)	0.2147(5)	5.45
C(9)	0.1303(5)	0.9801(13)	0.2763(6)	5.33
C(11)	0.1928(2)	0.8703(8)	0.2851(4)	4.42
C(12)	0.2082(2)	0.7483(8)	0.2940(4)	4.56
C(14)	0.1889(2)	0.5404(8)	0.2737(4)	5.00
C(15)	0.1183(3)	0.4865(8)	0.2809(5)	5.92
C(17)	0.0711(2)	0.6403(9)	0.2941(4)	5.01
C(18)	0.0631(3)	0.7669(9)	0.2805(4)	5.24
C(20)	0.0719(4)	0.9209(13)	0.2050(7)	5.49
C(7′)	1.0840(7)	0.9289(24)	0.1644(12)	4.48
C(9′)	1.1542(8)	0.9886(26)	0.2047(13)	4.84
C(20′)	1.1012(8)	0.9629(24)	0.2752(12)	4.48
N(8)	0.0999(3)	1.1257(9)	0.2066(6)	7.56
O(81)	0.0814(4)	1.1733(9)	0.2387(6)	12.74
O(82)	0.1124(4)	1.1810(9)	0.1706(6)	12.09
Anions				
S(A1)	0.1555(1)	0.6090(2)	0.4147(1)	5.94
S(A2)	0.1357(1)	0.8703(2)	0.4192(1)	5.84
C(A1)	0.1578(3)	0.7443(7)	0.4483(4)	3.97
N(A1)	0.1782(2)	0.7479(6)	0.5010(3)	4.50
C(A2)	0.1989(3)	0.6484(9)	0.5288(4)	5.53
C(A3)	0.1829(4)	0.8600(9)	0.5368(4)	6.47
C(A4)	0.2240(4)	0.7040(10)	0.5792(5)	7.44
C(A5)	0.2029(5)	0.8124(12)	0.5920(5)	9.08
S(B1)	0.2394(1)	0.6055(2)	0.1537(1)	5.60
S(B2)	0.2290(1)	0.8718(2)	0.1366(1)	5.95
C(B1)	0.2498(2)	0.7382(7)	0.1229(4)	3.98
N(B1)	0.2774(2)	0.7376(6)	0.0865(3)	4.00
C(B2)	0.3009(3)	0.6312(8)	0.0740(4)	5.44
C(B3)	0.2893(3)	0.8438(8)	0.0565(4)	5.70
C(B4)	0.3309(4)	0.6841(10)	0.0390(6)	9.78
C(B5)	0.3198(3)	0.8012(9)	0.0198(5)	7.12
S(C2)	0.0152(1)	0.7143(4)	0.1211(2)	9.05
S(C1)	0.0385(1)	0.4623(4)	0.1541(2)	9.15
C(C1)	0.0084(3)	0.5643(14)	0.1162(5)	7.56
N(C1)	−0.0221(3)	0.5253(14)	0.0799(5)	9.39
C(C2)	−0.0324(4)	0.4015(19)	0.0725(7)	11.52
C(C3)	−0.0490(4)	0.6034(17)	0.0442(6)	6.75
C(C4)	−0.0723(5)	0.3966(23)	0.0388(11)	13.64
C(C5)	−0.0720(6)	0.5213(27)	0.0050(8)	13.41
Solvent				
O(1)	0.0000	0.2842(41)	0.2500	23.52
O(2)	0.4171(5)	0.4841(18)	0.9764(8)	23.52
O(3)	0.0164(10)	0.0599(32)	0.3175(16)	23.52
O(4)	0.4622(6)	0.3495(20)	0.9091(9)	23.52
O(5)	0.0449(18)	0.1210(60)	0.9523(28)	23.52
O(6)	0.0186(11)	0.1188(36)	0.4945(17)	23.52
O(7)	0.0000	0.0260(51)	0.2500	23.52
O(8)	0.4727(21)	0.1925(59)	0.7069(32)	23.52
O(9)	0.0279(14)	0.0054(52)	0.4102(25)	23.52
O(10)	0.0561(21)	0.1102(62)	0.3731(32)	23.52

[a]Primed atoms represent non-common atoms of the minor contributor.

Crystal Data

$C_{29}H_{64}CoN_{11}O_9S_6$, $M = 962.2$, monoclinic, space group $C2/c$ (C^6_{2h}, No. 15), $a = 34.526(7)$, $b = 11.071(2)$, $c = 23.445(3)$ Å, $\beta = 96.37(1)°$, $U = 8907$ Å^3, D_c ($Z = 8$) = 1.435 g cm^{-3}, $F(000) = 4080$, $\mu_{Mo} = 5.56$ cm^{-1}. Specimen 0.31 X 0.18 X 0.08 mm, $2\theta_{max} = 45°$, $N = 4433$, N_o ($I > 2.5\sigma(I)$) = 2754, $N_v = 495$, $R = 0.065$, $R_w = 0.068$.

Programs used were SUSCAD [6] for data reduction, SHELX 76 [7] for refinement and ORTEP [8] for plotting. Scattering factors and anomalous dispersion terms were taken from ref. 9.

Results and Discussion

Synthesis

Compounds **1**–**3** were each found to be very soluble in chloroform, methylene chloride and toluene to give dark red solutions and were moderately soluble in ethanol, acetonitrile and acetone, the solubility increasing along the series $(CH_2)_4 < Et_2 <$ i-Pr$_2$. Addition of acids, HX, to solutions of these compounds results in decomposition of the dithiocarbamate anion and precipitation of the salt [Co(diNOsar)]X_3; providing a very convenient route to a wide range of different salts.

Structural Studies

The structure of **1** consists of the complex cation, three dithiocarbamate anions and five water molecules disordered over 10 sites. The structure confirms that the $[S_2CN(CH_2)_4]^-$ molecules are present as

TABLE 3. Relevant Bond Lengths (Å) and Angles (°) for 1

Co–N(3)	1.95(1)	Co–N(3′)	1.97(2)	N(10)...N(16)	2.92(2)
Co–N(6)	1.96(1)	Co–N(6′)	1.99(2)	N(6)...N(13)	2.90(2)
Co–N(10)	1.98(1)	Co–N(10′)	2.03(2)	N(3)...N(19)	2.87(2)
Co–N(13)	1.98(1)	Co–N(13′)	1.98(2)		
Co–N(16)	1.98(1)	Co–N(16′)	1.94(2)		
Co–N(19)	1.95(1)	Co–N(19′)	1.97(2)		

Anion geometries	Ligand A	Ligand B	Ligand C
S(1)...S(2)	3.01(1)	2.99(1)	2.98(1)
S(1)–C(1)	1.69(1)	1.70(1)	1.72(1)
S(2)–C(1)	1.70(1)	1.69(1)	1.68(1)
C(1)–N(1)	1.35(1)	1.35(1)	1.35(2)
N(1)–C(2)	1.43(1)	1.48(1)	1.42(3)
N(1)–C(3)	1.49(1)	1.45(1)	1.46(2)
C(2)–C(4)	1.52(2)	1.51(2)	1.51(2)
C(3)–C(5)	1.49(2)	1.51(2)	1.46(3)
C(4)–C(5)	1.45(2)	1.41(2)	1.59(4)
S(1)–C(1)–S(2)	123.2(5)	124.2(5)	122.9(5)
C(2)–N(1)–C(3)	111.5(7)	110.9(8)	111.5(11)

uncomplexed, unhydrated anions. As was found for the compound [Co(AMMEsar)][S_2CNEt_2]$_3$ [1], each dithiocarbamate anion approaches the D_3 cation along each of the C_2 axes and bonds via symmetrical pairs of hydrogen bonds between the sulfur atoms and the amine protons, effectively surrounding the cation (Figs. 1 and 2). In these compounds, the average intramolecular S...S distance of 2.99 Å is closely matched by the corresponding N...N distance of 2.90 Å with the S...N distances ranging between 3.05 and 3.26 Å. Despite major differences in the S...H hydrogen bonding network, the geometries of each of the anions (Table 3) are similar to those observed for the analogous hydrated systems: Li[$S_2CN(CH_2)_4$]·4H_2O [10], Na[$S_2CN(CH_2)_4$]·2H_2O [11] and [$(CH_2)_4NH_2$][$S_2CN(CH_2)_4$] [12].

The complex cation is disordered over two sites with occupancies 2/3:1/3. This disorder results from the two enantiomers occupying the same site, a

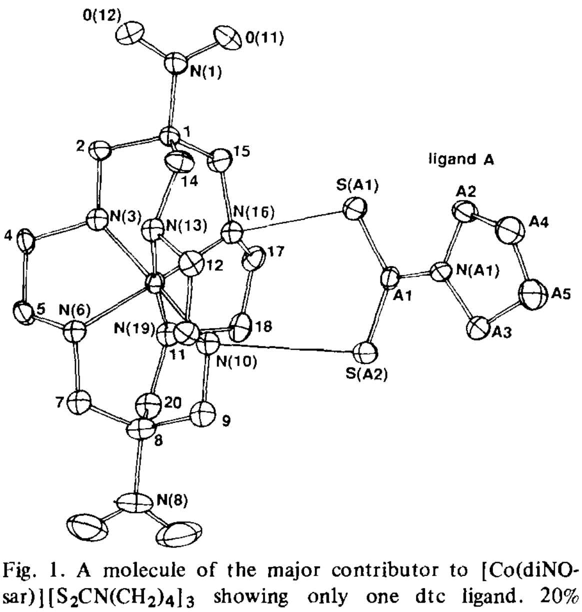

Fig. 1. A molecule of the major contributor to [Co(diNOsar)][$S_2CN(CH_2)_4$]$_3$ showing only one dtc ligand. 20% thermal ellipsoids are shown in this and the following Figure.

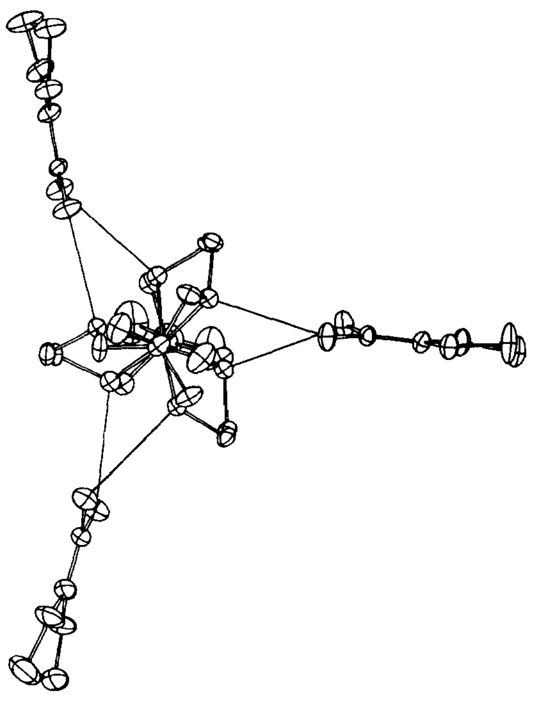

Fig. 2. A molecule of the major contributor viewed down the C_3 C_1–Co–C_8 axis of the molecule.

situation which is similar to that observed in the structure of the cage complex [Co(azacapten)]-$(ClO_4)_2$ [13]. Atoms on the cap-to-cap axis of the complex, the two nitro groups and the three atoms [C(2), C(14), C(15)] of one of the caps are common to both contributors to the disorder. Minor sites were observed for the nitrogen donor atoms and the remaining cap atoms [C(7), C(9), C(20)]. Despite this disorder, the amine hydrogen atom positions are approximately the same for the two contributors and thus the hydrogen bonding interactions with the dithiocarbamate anions are preserved. Five conformations of the diNOsar complex are possible: D_3lel_3, C_3lel_3, D_3ob_3, C_2lel_2ob, and C_2ob_2lel, where the first term describes the overall symmetry of the complex and the second denotes the orientation of the carbon–carbon vector of the ethylenediamine rings as either parallel to (*lel*) or at an angle to (*ob*) the C_3 cap-to-cap axis of the complex. In the present case, both contributors to the disorder have C_3lel_3 conformations with a torsion angle C(14)–C(1)–C(8)–C(20) of 166° rather than the 180° expected for the D_3lel_3 conformation. The conformation adopted is probably a consequence of the cation–anion hydrogen bonding environment since in the lel_3 conformation, each of the NH hydrogens lies parallel to the C_2 axes of the cation and directed towards the sulfur atoms of the anion. Metal–nitrogen bond lengths do not appear to be affected, however, since they average 1.97(2) Å, close to values observed in similar structures [14].

X-ray Photoelectron Spectroscopy

Co $2p_{3/2}$ binding energies range between 780 and 783 eV for Co(III) complexes [5] and for CoN_6 compounds such as $[Co(en)_3]Cl_3$ and $[Co(NH_3)_6]$-Cl_3, we have recorded values of 780.5 and 781.8 eV (*cf.* lit. 780.2 and 781.7 eV [15]). In the present study, *BE*s of 780.5, 780.4, 780.6 and 780.5 eV have been recorded for compounds **1**–**3** and for [Co(diNOsar)]Cl_3 (**4**); similar to the value found for the uncaged compound, $[Co(en)_3]Cl_3$. By contrast, for the CoS_6 dithiocarbamate complexes, the Co $2p_{3/2}$ *BE* decreases by 1.4 eV to an average value of 779.2 eV, a result which is consistent with the increasing effectiveness of these sulfur ligands in transferring electron density to the metal atom [16].

The S 2p binding energies for the dithiocarbamate moieties also differ significantly in the anionic and chelated forms. For compounds **1**–**3** and **5**–**7**, this *BE* ranged between 160.8 and 161.3 eV (average value 161.1 eV) whereas in the complexes **8**–**10**, it increased to an average value of 162.0 eV; this increase being consistent with the observed decrease in the *BE* of the central cobalt atom. We have noted elsewhere, that the formation of adducts of $Co(S_2$-$CN(CH_2)_4)_3$ with copper(I) halides results in a further small increase in the S 2p *BE* to 162.5 eV [17]. It has been reported previously that the S 2p *BE* values and hence the charge density on the sulfur atoms in dithiocarbamate salts and complexes, is affected by the substituent R groups [18] and in the present study the three ligands used were chosen to span the range of ligand field strengths attainable by this class of ligand [19, 20]. While our results show a consistent increase in this *BE* with ligand field strength, the magnitude of the change is only of the order of 0.2 eV, and approaching the error limits inherent in our experimental conditions. In these compounds, it was not possible to distinguish between the N 1s binding energies of the N-alkyl nitrogen atoms on the cation and the anion with *BE*s ranging unsystematically between 399.2 and 399.8 eV. However, the N-nitro nitrogen atoms were clearly characterized with a *BE* of 405.3 eV.

Supplementary Material

Non-hydrogen thermal parameters, the derived hydrogen positions, ligand non-hydrogen geometries and tables of calculated and observed structure factors are available from the authors on request.

Acknowledgements

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