Tetracyanoquinodimethane derivatives of fully condensed schiff base ligands derived from 2,6-diacetylpyridine: crystal structure of a nickel(ii) chloride complex with 2,6-diacetylpyridinebis(semicarbazone)

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TETRACYANOQUINODIMETHANE DERIVATIVES OF FULLY CONDENSED SCHIFF BASE LIGANDS DERIVED FROM 2,6-DIACETYLPYRIDINE: CRYSTAL STRUCTURE OF A NICKEL(II) CHLORIDE COMPLEX WITH 2,6-DIACETYLPYRIDINEBIS(SEMICARBAZONE)

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The ligands 2,13-dimethyl-3,6,9,12,18-pentaaza-bicyclo[12.3.1]octadeca-1(17),2,12,14(18),15-pentaene (L_1) and 2,6-diacetylpyridinebis(semicarbazone) (L_2) give pentagonal bipyramidal complexes with some transition metal ions. The structure of $[Ni-L_2(H_2O)_2]Cl_2 \cdot 2H_2O$ has been determined by single-crystal X-ray methods. Further reaction of complexes of L_1 and L_2 with the lithium salt of 7,7′,8,8′,-tetracyanoquinodimethane (tcnq) gives the corresponding adducts.

Keywords: Schiff base; Diacetylpyridine; Semicarbazone; Tetracyanoquinodimethane; Pentagonal bipyramid; X-ray structure

INTRODUCTION

Macrocyclic polyaza ligands have been used extensively [1] as donors in electron-transfer reactions with 7,7′,8,8′,-tetracyanoquinodimethane (tcnq) and other related acceptor compounds. Many of these compounds have interesting physical properties [2]. The nature of the donor atoms as well as the molecular geometry and planarity of the metal chelates serve to alter electrical properties and magnetism of corresponding tcnq derivatives [3]. We recently reported [4–6] synthetic and structural aspects of tcnq derivatives of some macrocyclic ligand transition metal chelates with various geometries at the metal centre. Literature reports [7–10] reveal the rare occurrence of pentagonal bipyramidal geometry in such coordination complexes. Of all known complexes of transition elements with pentagonal bipyramidal geometry, planar pentadentate ligands have been used.

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Schiff base ligands derived from 2,6-diacetylpyridine (DAP) have long been of interest. In particular, the condensation of DAP with easily available amine components has furnished potentially useful ligand systems for making a variety of charge transfer complexes [11]. Our interest in macrocyclic and open-chain Schiff base ligands of the type L_1 and L_2 has led us to synthesise transition metal complexes with pentagonal bipyramidal geometries. Further the planar chelates have been utilized to obtain donor acceptor adducts with tcnq, and these exhibit interesting properties.

L_1 L_2
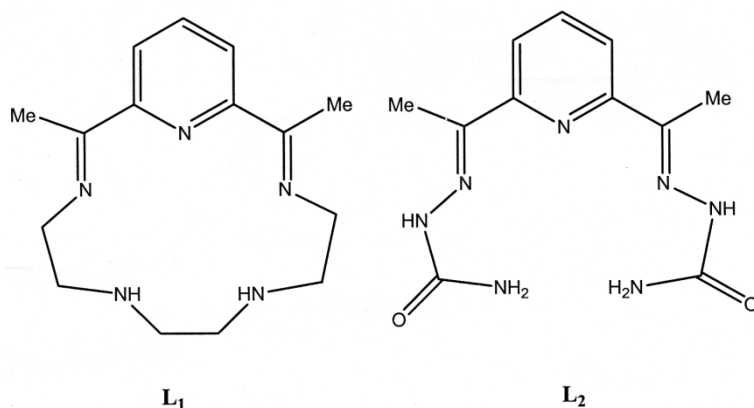
We now describe the synthesis and properties of Fe(III) complexes of L_1 and their adducts with tcnq. Mn(II), Fe(III), Ni(II) and Cu(II) complexes of ligand L_2 and their adducts with tcnq have been reported elsewhere [5]. We also report the crystal structure of one of the Ni(II) complexes.

EXPERIMENTAL

All reactions were carried out under atmosphere of dry nitrogen and the solvents were dried and degasified before use. The IR spectra were recorded as KBr pellets on a PYE UNICAM SP3-300 IR spectrophotometer. The UV-VIS spectra were recorded on a Shimadzu Graphicord 240 UV-VIS spectrophotometer. ESR and magnetic susceptibilities of complexes were recorded at the University of Manchester, UK. Litcnq, L_1 and L_2 and the precursor complexes $[FeL_1(ClO_4)]_2O(ClO_4)_2 \cdot H_2O$ and $[FeL_1(NCS)_2](ClO_4)$ were prepared by the reported methods [10,12,13] and their purities were checked by elemental analyses.

Syntheses

$[FeL_1(ClO_4)_2](tcnq)_2$ (1)

A solution of Litcnq (0.077 g, 3.67 mmol) in methanol (15 cm^3) was added dropwise to a stirred solution of $[FeL_1(ClO_4)]_2O(ClO_4)_2 \cdot H_2O$ (0.10 g, 0.067 mmol) in a methanol : water (1 : 1, 15 cm^3) mixture. The mixture was stirred at room temperature for 5 h and the solvent was removed under reduced pressure, leaving a dark blue residue. This was filtered, washed with diethyl ether (anhydrous) and dried *in vacuo*.

Yield 54%. *Anal*. Calc. for $FeC_{39}H_{31}N_{13}Cl_2O_8$ (%): C, 50.0; H, 3.3; N, 19.4; Found: C, 49.2; H, 2.9; N, 20.3.

[FeL$_1$(NCS)$_2$](tcnq) (2)

A solution of Litcnq (0.040 g, 1.90 mmol) in methanol (15 cm^3) was added to a stirred solution of $[FeL_1(NCS)_2](ClO_4)$ (0.100 g, 0.184 mmol) in methanol (15 cm^3). The reaction mixture was stirred at room temperature for 5 h and the solvent was removed under reduced pressure, leaving a brownish yellow residue. This was filtered, washed with methanol and then diethyl ether (anhydrous) and dried *in vacuo*. Yield 56%. *Anal*. Calc. for $FeC_{29}H_{27}N_{11}S_2$ (%): C, 53.6; H, 4.16; N, 23.7; Found: C, 52.4; H, 3.9; N, 22.8.

[NiL$_2$(H$_2$O)$_2$]Cl$_2$·2H$_2$O (3)

A solution of $NiCl_2 \cdot 6H_2O$ (0.318 g) in ethanol : water (4 : 1, 20 cm^3) mixture was added to a stirred suspension of L_2 (0.370 g) in ethanol : water (4 : 1, 25 cm^3) mixture. The reaction mixture was refluxed at 70–80°C for 4 h resulting in the separation of pale green product. This was filtered off and washed with ethanol then diethyl ether. Yield 70%. *Anal*. Calc. for $NiC_{11}H_{23}Cl_2N_7O_6$ (%); C, 27.5; H, 4.8; N, 20.4; Found C, 27.2; H, 4.5; N, 20.2.

Crystallography

Crystals of Complex (**3**) were grown by slow evaporation of a solution in ethanol : water (1 : 1) mixture. Only one form of crystals of (**3**) as green plates were obtained in contrast to the two forms of crystals of stoichiometry $NiL_2(NO_3) \cdot 3H_2O$ obtained [10] in a similar reaction.

Crystal Data $C_{11}H_{23}Cl_2N_7NiO_6$, green needles, *Mr* 478.97, triclinic, $a = 12.252(1)$, $b = 12.426(1)$, $c = 7.279(1)$ Å, $\alpha = 70.804(1)$, $\beta = 84.815(1)$, $\gamma = 72.232(1)°$, $U = 996.53(17)$ Å, $Z = 8$, $Dc = 1.596$ Mg m^{-3}.

Summary data collection conditions are as follows. Siemens SMARTCCD area detector and 0.3° φ scans. Index ranges $-14 \leq h, \leq 15, -12 \leq k \leq 15, -3, \leq l, \leq 9$. Reflections collected 6904; independent reflections $= 3705$ [R(int) $= 0.014$], completeness of data $= 91.2\%$, Refinement method full-matrix least-squares on F^2 (SHELXL 93). Data restrains parameters 3705/0/280; goodness-of-fit on F^2 1.067, Final R indices [$1.2\sigma(I)$] $R1 = 0.0270$, $wR_2 = 0.0758$; R indices (all data) $R1 = 0.0312$, $wR_2 = 0.0783$. Largest difference peak and hole 0.264 and -0.445 (eÅ^{-3}).

RESULTS AND DISCUSSION

Iron Complexes

Reaction of $[FeL_1(ClO_4)]_2O(ClO_4)_2 \cdot H_2O$ with Litcnq furnished $[FeL_1(ClO_4)_2](tcnq)_2$ (**1**) whereas reaction of $[FeL_1(NCS)_2](ClO_4)$ with Litcnq gave $[FeL_1(NCS)_2](tncq)$ (**2**). The stability of the pentagonal bipyramidal geometry around a variety of transition metal centres provided by the planar pentadentate ligands leads to the replacement of

uncoordinated anions [7,8,13–17]. In contrast to the precursor complex, $[FeL_1(ClO_4)]_2$ $O(ClO_4)_2 \cdot H_2O$, the IR spectrum of (**1**) does not show any band at $790 \, cm^{-1}$ attributed to Fe–O–Fe which indicates the formation of a monomeric complex rather than bridged dimer. Moreover the appearance of a split band at $1100–1200 \, cm^{-1}$ shows the presence of only coordinated ClO_4^- indicating that uncoordinated ClO_4^- has been replaced by tcnq$^-$. Extensive IR spectroscopic studies [2,18] of tcnq salts have demonstrated that IR spectra provide significant information on charge occupation and intermolecular interactions. Also the number and frequencies of the IR bands of tcnq are indicative of its oxidation state and coordination status. While $\nu(C{\equiv}N)$ bands indicate the presence or absence of coordinated tcnq groups $\delta(C–H)$ bands in the $800–880 \, cm^{-1}$ regions provide information about the presence of tcnq species in different oxidation states [18,19]. Both tcnq^0 and tcnq$^-$ exhibit characteristic $\delta(C–H)$ absorption at 863 and $828 \, cm^{-1}$, respectively, with corresponding $C{\equiv}N$ stretching at 2228 and $2181 \, cm^{-1}$, respectively. IR spectra of complexes containing both tcnq^0 and tcnq$^-$ exhibit broad bands at frequencies intermediate between those of tcnq^0 and tcnq$^-$ [20,21]. The $\nu(C{\equiv}N)$ mode in Complex (**1**) appears as a strong band at $2200 \, cm^{-1}$ indicating the uncoordinated status of tcnq. The appearance of a single broad band at $800–835 \, cm^{-1}$ indicates the presence of mixed species tcnq^0 and tcnq$^-$. Not unexpectedly, the electronic spectrum of the tcnq complexes shows two transitions for tcnq groups [22], the locally excited levels LE_1 at 842 nm and LE_2 at 394 nm being characteristic of the free anion radical. Since neutral tcnq shows a band at 394 nm only, the ratio of the two bands, $\varepsilon(394)/\varepsilon(842)$, indicates the oxidation state of the tcnq groups present [23]. A ratio less than 1.0 (*ca* 0.5–0.8) indicates the presence of tcnq$^-$ whereas one greater than 1.0 shows the additional presence of tcnq^0. The observed intensity ratio $\varepsilon(394)/\varepsilon(842) = 1.2$ in Complex (**1**) shows the presence of tcnq^0 and tcnq$^-$. The FAB mass spectrum of (**1**) shows a molecular ion peak at 936 corresponding to the formula $[FeL_1(ClO_4)_2](tcnq)_2$. Peaks at m/z 731 and 527 are assigned to $\{[FeN_5(ClO_4)_2][tcnq]\}^+$ and $[FeN_5(ClO_4)]^+$ which further indicates the monomeric nature of the complex. The room temperature magnetic moment (4.47 BM) of (**1**) indicates the presence of high spin Fe(III) with a strong antiferromagnetic interaction with the unpaired spin on tcnq$^-$, the presence of which has further been corroborated by the EPR spectrum of the complex which shows a sharp signal at $g = 2.002$ in powder as well as in frozen solution (attributable to tcnq$^-$). A very broad signal corresponding to Fe(III) is observed at approximately 3300 G. A pentagonal bipyramidal structure with five equatorial sites occupied by five nitrogen atoms of the macrocyclic ligand and the two axial sites by ClO_4^- ions is thus suggested for (**1**) with tcnq remaining uncoordinated.

Reaction of $[FeL_1(NCS)_2](ClO_4)$ with Litcnq gave (**2**). The IR spectrum of (**2**) shows a strong band at $2000 \, cm^{-1}$ assigned to $\nu_{asym}(NCS)$. It was not possible to assign $\nu_{sym}(NCS)$ because tcnq bands appear in the same region ($800–850 \, cm^{-1}$). A strong, unsplit band due to $\nu(C{\equiv}N)$ of tcnq$^-$ appears at $2180 \, cm^{-1}$, further supported by the appearance of $\delta(C–H)$ at $830 \, cm^{-1}$. This is in good agreement with the data obtained for $[n\text{-}Bu_4N](tcnq)$ [24]. The electronic spectrum of (**2**) is somewhat different from that of (**1**). The intensity ratio $\varepsilon(394)/\varepsilon(842)$ is 1.0, corresponding neither to the value 1.25 for $(tcnq)_3^{2-}$ nor 2.0 for the formulation $(tcnq)_2^-$. Therefore we cannot rule out the presence of small amounts of tcnq^0 present as an impurity resulting from the oxidation of tcnq$^-$ by ferric ions in solution [25]. The FAB mass spectrum shows the molecular ion peak at m/z 648. Other peaks corresponding to $[FeL_1(NCS)_2]^+$, $[FeL_1(NCS)]^+$ and $[FeL_1]^+$ are observed at m/z 445, 387 and 329, respectively, pointing

to the monomeric nature of (**2**) in a manner similar to (**1**). The room temperature magnetic moment of 7.0 BM is greater than the expected value for high spin Fe(III). A very sharp signal at $g = 2.00$ is seen in the powder EPR spectrum of the complex and this further supports the presence of tcnq$^-$ [26]. The powder EPR spectrum also shows a broad resonance at *ca* 3320 G with a *g* value of 2.03. The large line width suggests the presence of Fe(III). On the basis of the above evidence, a pentagonal bipyr-amidal structure with five equatorial sites occupied by the five nitrogen atoms of the macrocyclic ligand and the two axial sites by *N*-coordinated thiocyanate groups is suggested. The tcnq$^-$ remains uncoordinated in Complex (**2**) [13,14,27].

Nickel Complex

Reaction of $NiCl_2 \cdot 6H_2O$ with ligand L_2 gave $[NiL_2(H_2O)_2]Cl_2 \cdot 2H_2O$ (**3**). In the IR spectrum of the ligand L_2, the characteristic carbonyl frequency of 2,6-diacetylpyridine, $\nu(C{=}O)$ (*ca* 1700 cm^{-1}), disappears in the complex and a strong band appears at 1680 cm^{-1}, indicating the formation of imine [28]; $\nu(N{-}H)$ and $\nu(C{=}O)$ of the semicar-bazide moiety of the ligand appear at 3000–3500 cm^{-1} and 1605 cm^{-1}, respectively. A strong band at 1660 cm^{-1} is attributed to $\nu(C{=}N)$. The appearance of $\nu(C{=}N)$ at relatively lower frequency indicates the coordination of the imine nitrogen to the metal centre. The $\nu(N{-}H)$ region at 3100–3500 cm^{-1} showed two to three broad bands of variable intensity indicating the overlapping with water absorptions.
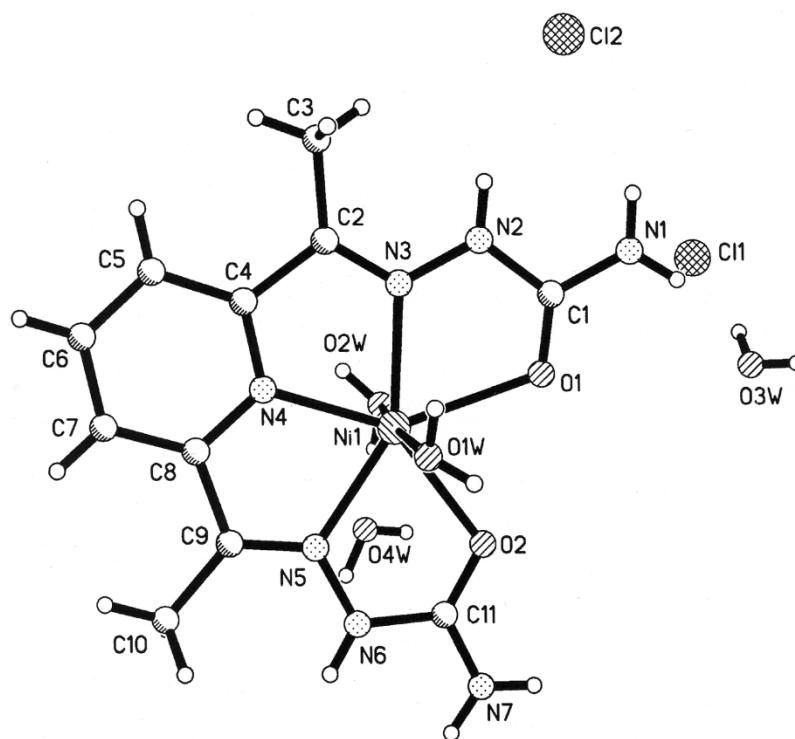

FIGURE 1   ORTEP diagram and atomic numbering of $[NiL_2(H_2O)_2]Cl_2 \cdot H_2O$ (**3**).

Rocking or wagging modes of coordinated water molecules appear as a medium to broad band at $520 \, cm^{-1}$. An ORTEP drawing of (**3**) is shown in Fig. 1 and the coordination geometry is shown as pentagonal bipyramidal. The five equatorial sites of a planar pentagon are occupied by three nitrogen and two oxygen atoms from the planar N_3O_2 ligand and the two water molecules lead to pentagonal bipyramidal stereochemistry about the central metal atom. Data concerning bond lengths, bond angles and atomic coordinates are given in Tables I–III. The chemistry of its adduct with tcnq along with other complexes has been published elsewhere [5].

TABLE I Bond lengths (Å) for the complex $[NiL_2(H_2O)_2]Cl_2 \cdot 2H_2O$

Ni(1)–O(1W)	2.0445(15)	C(2)–C(3)	1.495(3)
Ni(1)–N(4)	2.0610(15)	N(4)–C(4)	1.340(2)
Ni(1)–O(2W)	2.0620(14)	N(4)–C(8)	1.342(2)
Ni(1)–N(5)	2.1534(16)	C(4)–C(5)	1.389(3)
Ni(1)–N(3)	2.1689(16)	N(5)–C(9)	1.281(3)
Ni(1)–O(2)	2.3222(15)	N(5)–N(6)	1.358(2)
Ni(1)–O(1)	2.3837(15)	C(5)–C(6)	1.384(3)
O(1)–C(1)	1.226(2)	N(6)–C(11)	1.378(3)
N(1)–C(1)	1.339(3)	C(6)–C(7)	1.385(3)
C(1)–N(2)	1.375(3)	N(7)–C(11)	1.337(3)
O(2)–C(11)	1.235(2)	C(7)–C(8)	1.389(3)
N(2)–N(3)	1.363(2)	C(8)–C(9)	1.486(3)
C(2)–N(3)	1.283(3)	C(9)–C(10)	1.499(3)
C(2)–C(4)	1.487(3)		

TABLE II Bond angles (°) for the complex $[NiL_2(H_2O)_2]Cl_2 \cdot 2H_2O$

O(1W)–Ni(1)–N(4)	93.44(6)	N(3)–C(2)–C(3)	125.60(18)
O(1W)–Ni(1)–O(2W)	172.23(6)	C(4)–C(2)–C(3)	121.20(18)
N(4)–Ni(1)–O(2W)	94.31(6)	C(2)–N(3)–N(2)	121.49(16)
O(1W)–Ni(1)–N(5)	90.89(6)	C(2)–N(3)–Ni(1)	118.77(13)
N(4)–Ni(1)–N(5)	73.96(6)	N(2)–N(3)–Ni(1)	119.54(12)
O(2W)–Ni(1)–N(5)	91.89(6)	C(4)–N(4)–C(8)	120.77(16)
O(1W)–Ni(1)–N(3)	89.93(6)	C(4)–N(4)–Ni(1)	119.64(13)
N(4)–Ni(1)–N(3)	73.96(6)	C(8)–N(4)–Ni((1)	119.56(13)
O(2W)–Ni(1)–N(3)	91.56(6)	N(4)–C(4)–C(5)	121.24(18)
N(5)–Ni(1)–N(3)	147.90(6)	N(4)–C(4)–C(2)	114.35(17)
O(1W)–Ni(1)–O(2)	88.99(6)	C(5)–C(4)–C(2)	124.41(18)
N(4)–Ni(1)–O(2)	144.61(6)	C(9)–N(5)–N(6)	121.99(16)
O(2W)–Ni(1)–O(2)	85.08(6)	C(9)–N(5)–Ni(1)	119.20(13)
N(5)–Ni(1)–O(2)	70.70(6)	N(6)–N(5)–Ni(1)	118.72(12)
N(3)–Ni(1)–O(2)	141.40(6)	C(6)–C(5)–C(4)	118.14(19)
O(1W)–Ni(1)–O(1)	86.26(6)	N(5)–N(6)–C(11)	115.14(16)
N(4)–Ni(1)–O(1)	143.59(6)	C(5)–C(6)–C(7)	120.57(16)
O(2W)–Ni(1)–O(1)	87.11(6)	C(6)–C(7)–C(8)	118.29(19)
N(5)–Ni(1)–O(1)	142.43(6)	N(4)–C(8)–C(7)	120.99(18)
N(3)–Ni(1)–O(1)	69.63(6)	N(4)–C(8)–C(9)	113.95(16)
O(2)–Ni(1)–O(1)	71.79(5)	C(7)–C(8)–C(9)	125.06(18)
C(1)–O(1)–Ni(1)	113.88(13)	N(5)–C(9)–C(8)	113.20(17)
O(1)–C(1)–N(1)	124.3(2)	N(5)–C(9)–C(10)	125.10(19)
O(1)–C(1)–N(2)	121.36(18)	C(8)–C(9)–C(10)	121.69(18)
N(1)–C(1)–N(2)	114.31(18)	O(2)–C(11)–N(7)	124.6(2)
C(11)–O(2)–Ni(1)	114.50(13)	O(2)–C(11)–N(6)	120.74(18)
N(3)–N(2)–C(1)	115.42(16)	N(7)–C(11)–N(6)	114.65(19)
N(3)–C(2)–C(4)	113.17(16)		

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	U(eq)
Ni(1)	2435(1)	1676(1)	2481(1)	32(1)
O(1W)	2444(2)	2113(1)	−484(2)	37(1)
O(1)	3050(1)	−349(1)	2535(3)	47(1)
N(1)	2404(2)	−1852(2)	2414(3)	51(1)
C(1)	2262(2)	−757(2)	2495(3)	35(1)
Cl(1)	3977(1)	−4305(1)	7503(1)	55(1)
O(2W)	2607(1)	1033(1)	5469(2)	36(1)
O(2)	4425(1)	1055(1)	2479(2)	43(1)
N(2)	1137(1)	−104(1)	2555(2)	34(1)
C(2)	−41(2)	1746(2)	2545(3)	30(1)
Cl(2)	−355(1)	−1815(1)	2358(1)	39(1)
O(3W)	4831(2)	−3249(2)	3266(4)	66(1)
N(3)	969(1)	1025(1)	2592(2)	29(1)
C(3)	−1137(2)	1473(2)	2445(3)	43(1)
O(4W)	4277(2)	1349(2)	7303(3)	44(1)
N(4)	1007(1)	3082(1)	2480(2)	27(1)
C(4)	−39(2)	2943(2)	2542(2)	29(1)
N(5)	3065(1)	3145(2)	2312(2)	31(1)
C(5)	−1019(2)	3862(2)	2588(3)	38(1)
N(6)	4214(1)	2978(2)	2233(3)	37(1)
C(6)	−888(2)	4934(2)	2562(3)	42(1)
N(7)	6005(2)	1657(2)	2475(4)	59(1)
C(7)	194(2)	5075(2)	2513(3)	39(1)
C(8)	1138(2)	4119(2)	2468(3)	30(1)
C(9)	2352(2)	4128(2)	2385(3)	32(1)
C(10)	2670(2)	5193(2)	2423(4)	48(1)
C(11)	4875(2)	1831(2)	2409(3)	37(1)

Acknowledgments

Supplementary Data

Full lists of crystallographic data are available from the authors upon request.

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