Chromium(II) Complexes of *o*-Phenylenediamine. The Crystal and Molecular Structures of Bis(*o*-phenylenediamine-κ*N*)-bis(thiocyanato-κ*N*)chromium(II) and Bis(*o*-phenylenediamine-κ²*N*,*N*′) bis(*o*-phenylenediamine-κ*N*)chromium(II) Trifluoromethanesulphonate†

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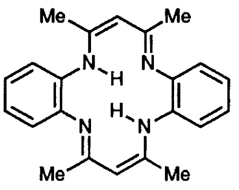
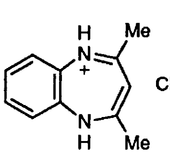
The following chromium(II) complexes of *o*-phenylenediamine (opd) have been isolated: $[Cr(opd)_2(NCS)_2]$, $[Cr(opd)_4]Br_2$, $[Cr(opd)_2I_2]\cdot1.5EtOH$, $[Cr(opd)Cl_2]$, $[Cr(opd)_6]Cl_2$ and $[Cr(opd)_4][CF_3SO_3]_2$. From the patterns of bands assigned to NH_2 and CN stretching vibrations in the infrared spectra the first two complexes contain monodentate diamine, the next two bidentate diamine and the last two both mono- and bi-dentate diamine; thus $[Cr(opd)_6]Cl_2$ is more correctly formulated as $[Cr(opd)_4]Cl_2\cdot2opd$. Crystal-structure determinations confirm the assignments for $[Cr(opd)_2(NCS)_2]$ and $[Cr(opd)_4][CF_3SO_3]_2$. The thiocyanato complex crystallises in the monoclinic space group $P2_1/c$ with a = 11.027(3), b = 5.828(2), c = 13.431(2) Å, β = 103.93(2)° and Z = 2. The structure was refined to R = 0.040 for 1551 observed reflections. There are *trans*-planar units in which the bond distances are Cr–NH_2 (monodentate diamine) 2.160(2) and Cr–NCS 2.036(2) Å, with S atoms of isothiocyanato groups of adjacent units in the axial positions, Cr–S 2.972(2) Å forming a thiocyanato-bridged structure. The triflate crystallises in the orthorhombic space group *Pbca*, with a = 8.978(8), b = 22.455(7), c = 16.842(2) Å and Z = 4. The structure was refined to R = 0.061 for 1863 observed reflections. The co-ordination sphere consists of two bidentate diamine molecules, mean Cr–N 2.119 Å, with two more distant, axially positioned, monodentate molecules at 2.669(5) Å. In accordance with its structure $[Cr(opd)_2(NCS)_2]$ exhibits antiferromagnetic behaviour as does $[Cr(opd)Cl_2]$ which is a chloride-bridged polymer. The triflate and the remaining complexes show simple paramagnetic behaviour (90–300 K). Attempts to prepare a chromium(II) complex of a tetraazamacrocyclic ligand by reaction of the *o*-phenylenediamine complexes with acetylacetone were unsuccessful; either no reaction took place or the benzodiazepinium chloride was isolated.

It is known[1] that the nickel(II) complex of the tetraaza macrocycle 6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11] tetraazacyclotetradecine (H_2L^1) can be prepared from nickel(II) acetate, *o*-phenylenediamine (opd) and acetylacetone. In attempts to prepare the corresponding chromium(II) tetraaza macrocycle, hydrated chromium(II) acetate was heated with opd and acetylacetone under reflux in various solvents but no reaction ensued, presumably due to the stability of the chromium–chromium bond in the dinuclear acetate.

Since the compound H_2L^1 is believed to form through the intermediate nickel(II) opd complexes, a number of chromium(II) opd complexes have been prepared and their reactions with acetylacetone investigated. In one case, a purple-black crystalline compound was isolated; unfortunately it did not contain chromium, and, although it was thought initially[2] to be a new octaazamacrocycle, it is now shown to be the 2,4-dimethyl-1,5-benzodiazepinium chloride L^2. This paper also reports the preparation and properties of the new chromium(II) opd complexes (Table 1) and the crystal and molecular structures of $[Cr(opd)_2(NCS)_2]$ and $[Cr(opd)_4][CF_3SO_3]_2$. Earlier workers[3–6] found that other bivalent transition-metal ions form a variety of complexes with one, two, three, four or six opd molecules, and deduced whether the diamine was mono- or bi-dentate mainly from the spectroscopic behaviour of the complexes. A later crystal-structure determination[7] on the nickel(II) complex, $[Ni(opd)_6]Cl_2$ showed that the correct formulation is $[Ni(opd)_4]Cl_2\cdot2opd$, with two bidentate equatorial ligands, two monodentate axial ligands and two lattice opd molecules rather than with six monodentate ligands as first proposed.[3]



H_2L^1



L^2

Experimental

Chromium metal (Aldrich, >99.99%) was used for the preparation of the hydrated chromium(II) halides[8] and trifluoromethanesulphonate (triflate) by dissolution of the metal in the appropriate acid. *o*-Phenylenediamine (Fluka, *purum* grade) was used as received as was the trifluoromethanesulphonic acid (Aldrich). All solvents were AnalaR grade and were degassed before use.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Analytical data

Complex	Colour	Analysis (%)*		
		C	H	N
$[Cr(opd)Cl_2]$	Pale blue	32.0	4.0	11.8
		(31.2)	(3.5)	(12.1)
$[Cr(opd)_2I_2]\cdot 1.5EtOH$	Purple	29.9	4.3	9.2
		(30.5)	(4.3)	(9.5)
$[Cr(opd)_2(NCS)_2]$	Purple	44.3	4.2	21.9
		(43.7)	(4.2)	(21.7)
$[Cr(opd)_4]Br_2$	Lilac	44.7	5.1	17.2
		(44.7)	(5.0)	(17.4)
$[Cr(opd)_4][CF_3SO_3]_2$	Purple	40.2	4.2	14.1
		(39.9)	(4.1)	(14.3)
$[Cr(opd)_6]Cl_2$	Lilac	55.2	6.2	21.5
		(55.7)	(6.2)	(21.7)

* Calculated values in parentheses.

Electronic spectra were recorded on a Beckman Acta MIV spectrophotometer fitted with a diffuse reflectance sphere with the samples in a sealed cell. Magnetic measurements were carried out on samples in sealed tubes by the Gouy method. The infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer.

Preparations.—All chromium(II) compounds were handled under nitrogen or vacuum and the solids were dried by direct pumping with an oil pump. The complexes were obtained in 40–60% yield.

Chromium(II) *trifluoromethanesulphonate tetrahydrate.* A mixture of trifluoromethanesulphonic acid (30 cm^3) and water (20 cm^3) was heated at 80–90 °C with chromium metal (4.7 g). After 15 min effervescence began, the solution turned blue and heating was continued for a total of 9 h. The solution was decanted from the unreacted metal, which was weighed, reheated to dissolve any crystals and allowed to cool slowly overnight. The pale blue platelets (1.5 g, 32%) obtained were filtered off and washed with dry diethyl ether. Alternatively, a nearly quantitative yield of pale blue powder can be obtained by concentrating the decanted liquid to dryness and washing with dry ether (Found: C, 5.9; H, 2.1. Calc. for $C_2H_8CrF_6O_{10}S_2$: C, 5.7; H, 1.9%). The compound rapidly turns green in air. The reflectance spectrum contains a very broad band asymmetric to low wavenumber at 14 500 cm^{-1}. Infrared data (KBr and Polythene plates, Nujol mull): 3380s (vbr), ν(OH); 1650m, δ(OH_2); 1270s, ν(SO_3); 1225s, ν(SO_3); 1185m, ν(CF); 1025m, ν(CF); 715m(br) and 630 m(br) cm^{-1}.

Diisothiocyanatobis(o-*phenylenediamine*)*chromium*(II). To $CrCl_2\cdot 4H_2O$ (1.44 g, 7.39 mmol) in deoxygenated water (25 cm^3) was added ammonium thiocyanate (1.12 g, 14.8 mmol) followed by aqueous opd (1.60 g, 14.8 mmol, 50 cm^3 water). On mixing a copious purple precipitate appeared. This was filtered off, washed with water and dried. Purple needles with the same analysis as the precipitate but suitable for crystallographic study separated from the filtrate.

Hexakis(o-*phenylenediamine*)*chromium*(II) *chloride.* When during unsuccessful attempts to obtain $[Cr(opd)_2Cl_2]$ stoichiometric quantities of the reactants were mixed in aqueous solution a flocculent, difficult-to-filter, blue-grey precipitate always formed first. From the filtrate purple crystals analysing as $[Cr(opd)_6]Cl_2$ were once obtained. Ligand-to-metal ratios of 4:1, 3:1 and 1:1 were also tried, but none yielded characterisable products from aqueous solution, and the ligand separated on cooling aqueous solutions in the freezer. The 6:1 complex was eventually isolated from ethanol. To chromium(II) chloride (0.14 g, 0.72 mmol) dissolved in absolute ethanol (20 cm^3) was added opd (0.47 g, 4.3 mmol) also in ethanol (20 cm^3). The pale blue suspension which formed immediately was placed in the freezer until the reaction mixture became lilac. The microcrystalline powder was filtered off quickly and dried. It was not washed as this removes opd. The compound should probably be formulated as $[Cr(opd)_4]Cl_2\cdot 2opd$ (see Results and Discussion).

Dichloro(o-*phenylenediamine*)*chromium*(II). When opd (5.03 g, 0.046 mol) in ethanol (110 cm^3) was added to $CrCl_2\cdot 4H_2O$ (4.53 g, 0.046 mmol) in the same solvent (20 cm^3) and the solution shaken vigorously a sky-blue precipitate formed. The flask was shaken intermittently during 1 h, and then the product was filtered off, washed with ethanol and dried.

Tetrakis(o-*phenylenediamine*)*chromium*(II) *bromide.* To opd (0.99 g, 9.15 mmol) in absolute ethanol (50 cm^3) was added $CrBr_2\cdot 6H_2O$ (1.47 g, 4.59 mmol). The blue solution was stirred at 60 °C for 30 min and then allowed to stand for several days. The dark pink crystals which separated were filtered off, washed with absolute ethanol, and dried. This reaction with 2 molar equivalents of opd gave a 4:1 product, but reaction with 4 or 6 molar equivalents gave respectively lilac-purple needles and a fine lilac powder. Neither product was characterised because each appeared to be a mixture.

Tetrakis(o-*phenylenediamine*)*chromium*(II) *trifluoromethanesulphonate.* The diamine (1.05 g, 9.71 mmol) in absolute ethanol (50 cm^3) was added to a pale blue solution of $Cr(H_2O)_4(CF_3SO_3)_2$ (0.56 g, 1.56 mmol) dissolved in absolute ethanol (50 cm^3). The resulting deep marine blue solution was heated to 70 °C, allowed to cool to room temperature and then placed in the freezer. Lilac needles suitable for X-ray study formed. These were filtered off, washed with cold absolute ethanol and dried.

Bis(o-*phenylenediamine*)*chromium*(II) *iodide.* When opd (2.07 g, 19.05 mmol) in ethanol (50 cm^3) was added to a turquoise solution of $CrI_2\cdot 6H_2O$ (1.32 g, 3.19 mmol) in ethanol a deep blue solution was formed from which a purple precipitate separated. This was filtered off, washed with cold ethanol and dried. This complex is an ethanol solvate (Table 1).

2,4-*Dimethyl*-1,5-*benzodiazepinium chloride.* When $[Cr(opd)_6]Cl_2$ (0.23 g, 0.30 mmol) was added under nitrogen to a solution of acetylacetone (0.06 g, 0.60 mmol) in acetonitrile (50 cm^3) a sandy brown solution and suspension formed. The mixture was heated with stirring until all the solid dissolved and the solution became deep maroon. The solution was allowed to cool and then kept at −20 °C overnight. The deep purple-black crystals obtained (which were not air-sensitive), were filtered off, dried and recrystallised from $CHCl_3$–hexane. When prepared from opd and acetylacetone in aqueous organic conditions[9] the product was a dihydrate. Prepared as above the product analysed as containing 0.25 mol water (Found: C, 62.0; H, 6.5; N, 13.2. Calc. for $C_{11}H_{13}ClN_2\cdot 0.25H_2O$: C, 62.0; H, 6.4; N, 13.1%). ^1H NMR data: (300 MHz, solvent $CDCl_3$; standard $SiMe_4$): δ 1.77 (s, 6 H, 2CH_3), 3.60 (s, 1 H, CH), 6.90, 7.10 (m, 4 H, aromatic), 10.37 (br s, 2 H, 2NH); these do not distinguish between the benzodiazepinium and macrocycle formulations. In the absence of mass spectrometric facilities a single crystal was investigated by X-ray diffraction which confirmed the benzodiazepinium structure.[10]

X-Ray Structure Determination of $[Cr(opd)_2(NCS)_2]$.—A crystal of $[Cr(opd)_2(NCS)_2]$ of approximate dimensions 0.1 × 0.1 × 0.5 mm was sealed in a Lindemann capillary under nitrogen. The unit-cell dimensions were determined by least-squares refinement of a set of 25 reflections ($13 \leqslant \theta \leqslant 15°$).

Crystal data. $C_{14}H_{16}CrN_6S_2$, $M = 384.45$, monoclinic, space group $P2_1/c$, $a = 11.027(3)$, $b = 5.828(2)$, $c = 13.431(2)$ Å, $\beta = 103.93(2)°$, $Z = 2$, $U = 837.7$ Å^3, $D_c = 1.524$ g cm^{-3}, $F(000) = 396$, graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\ 67$ Å), μ(Mo-Kα) = 9.1 cm^{-1}.

The intensity data were collected on an Enraf–Nonius CAD4 four-circle diffractometer in an ω–2θ scan mode in the range 1–26° covering the index ranges $0 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 7$, $-16 \leqslant l \leqslant 16$. 1919 Reflections were collected of which 1737 were considered to be unique and 1551 observed, *i.e.*

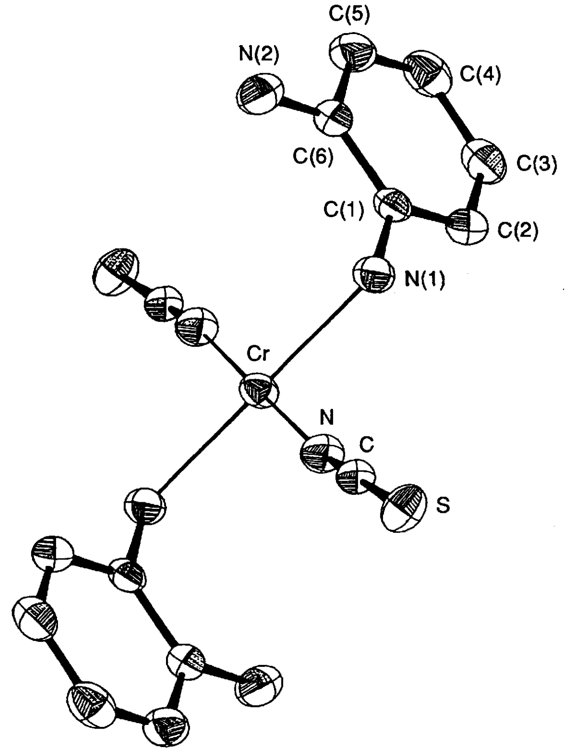

Fig. 1 Atom numbering scheme for [Cr(opd)$_2$(NCS)$_2$]

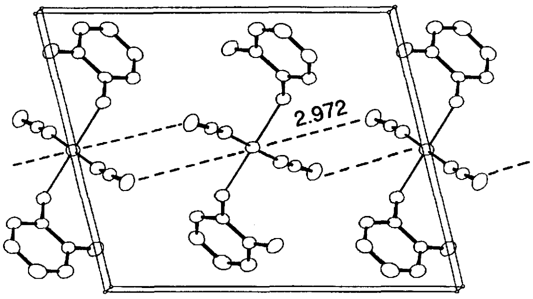

Fig. 2 The packing of the [Cr(opd)$_2$(NCS)$_2$] molecules along the *c* axis of the unit cell

$I \geqslant 3.0\sigma(I)$. A reference reflection measured every 60 min of exposed X-ray time showed no significant change in intensity (−0.3%). The crystals were found to be monoclinic, and an examination of the systematic absences indicated the space group to be $P2_1/c$. The data were corrected for Lorentz and polarisation effects and absorption (ψ-scan data).

Interpretation of the three-dimensional Patterson synthesis revealed the positions in the unit cell of the chromium and sulphur atoms. Conventional Fourier techniques then revealed the positions of all non-hydrogen atoms.

Isotropic refinement of non-hydrogen atoms converged at $R = 0.145$. Application of empirical absorption corrections by DIFABS[11] reduced R to 0.091. Anisotropic refinement initially for chromium and sulphur and then for all non-hydrogen atoms converged at $R = 0.044$. A Fourier difference map revealed the positions of the hydrogen atoms associated with the nitrogen atoms and the ring hydrogen atoms. These were added to the atoms list. Inclusion of the hydrogen atoms, which were refined isotropically, caused R to converge at 0.040; $R' = 0.058$, $S = 1.209$ using the weighting scheme:[12] $w^{-1} = [\sigma(F)]^2 + (0.4F)^2 + 4.0$.

The atom numbering scheme is shown in Fig. 1, and the packing of the [Cr(opd)$_2$(NCS)$_2$] molecules in the unit cell in Fig. 2. Final atomic parameters are given in Table 2 and bond lengths and angles in Table 3. The computations were carried out using the SDP-Plus V 1.1a suite of programs[13] on a DEC PDP 11/73 computer.

Table 2 Final atomic positions for [Cr(opd)$_2$(NCS)$_2$] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Cr	0.5	0	0.5
S	0.600 45(6)	0.710 3(1)	0.356 0(4)
N	0.558 1(2)	0.284 6(3)	0.437 0(1)
N(1)	0.329 3(2)	0.027 5(3)	0.381 2(2)
N(2)	0.144 9(2)	−0.023 5(4)	0.493 2(2)
C	0.576 4(2)	0.461 0(4)	0.403 9(2)
C(1)	0.242 0(2)	−0.161 6(4)	0.361 1(2)
C(2)	0.247 3(2)	−0.321 3(4)	0.285 8(2)
C(3)	0.165 3(3)	−0.504 8(4)	0.266 8(2)
C(4)	0.076 0(3)	−0.527 3(4)	0.322 8(2)
C(5)	0.070 5(2)	−0.368 8(5)	0.398 0(2)
C(6)	0.154 0(2)	−0.185 1(4)	0.419 3(2)

Table 3 Selected bond lengths (Å) and angles (°) in [Cr(opd)$_2$(NCS)$_2$] with e.s.d.s in parentheses

Cr–N	2.036(2)	N–Cr–N′	180.00(0)
Cr–N(1)	2.160(2)	N–Cr–N(1)	86.60(7)
S–C	1.638(2)	S–C–N	179.2(2)
N–C	1.158(3)		
N(1)–C(1)	1.448(3)	C(3)–C(4)	1.381(4)
C(6)–N(2)	1.389(3)	C(4)–C(5)	1.381(4)
C(1)–C(2)	1.386(3)	C(5)–C(6)	1.399(4)
C(2)–C(3)	1.387(4)	C(6)–C(1)	1.392(3)

X-Ray Structure Determination of [Cr(opd)$_4$][CF$_3$SO$_3$]$_2$.—A crystal of [Cr(opd)$_4$][CF$_3$SO$_3$]$_2$ of approximate dimensions 0.4 × 0.04 × 0.4 mm was sealed in a Lindemann capillary under nitrogen. The unit-cell dimensions were determined by a least-squares refinement of a set of 25 reflections ($11 \leqslant \theta \leqslant 15°$).

Crystal data. $C_{26}H_{32}CrF_6N_8O_6S_2$, $M = 782.7$, orthorhombic, space group *Pbca*, $a = 8.978(8)$, $b = 22.455(7)$, $c = 16.842(2)$ Å, $Z = 4$, $U = 3395.4$ Å^3, $D_c = 1.531$ g cm^{-3}, $F(000) = 1608$, graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\ 67$ Å), μ(Mo-Kα) = 5.3 cm^{-1}.

The intensity data were collected on an Enraf–Nonius CAD4 four-circle diffractometer in an ω–2θ scan mode in the range $1 \leqslant \theta \leqslant 25°$ covering an index range $0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 26$, $0 \leqslant l \leqslant 20$. 3390 Unique reflections were collected of which 1863 were considered to be observed, *i.e.* $I \geqslant 3.0\sigma(I)$. A reference reflection measured every 60 min of exposed X-ray time showed no significant change in intensity (−0.5%). The crystals were found to be orthorhombic, and an examination of the systematic absences indicated the space group to be *Pcab*. Since this is a non-standard space group a rotation matrix (001/010/100) was applied to give *Pbca*.

Interpretation of the three-dimensional Patterson synthesis yielded the position of the chromium in the unit cell, which was confirmed by the use of MULTAN. This also found the positions of all non-hydrogen atoms in the structure. Isotropic refinement of non-hydrogen atoms converged at $R = 0.107$. A Fourier difference map revealed the positions of the ring hydrogen atoms which were added to the atoms list. Four cycles of least-squares refinement with the ring hydrogens included, but not refined, lowered R to 0.105. Anisotropic refinement initially for chromium and sulphur, and then for all atoms (with the ring hydrogens fixed), converged at $R = 0.071$. A Fourier difference map gave the positions of the eight hydrogens associated with the nitrogen atoms. They were added to the atoms list. Inclusion of these hydrogens, which were refined isotropically, caused R to converge at 0.061; $R' = 0.091$ and $S = 1.268$ using the same weighting scheme as for [Cr(opd)$_2$(NCS)$_2$]. The atom numbering scheme is shown in Fig. 3.

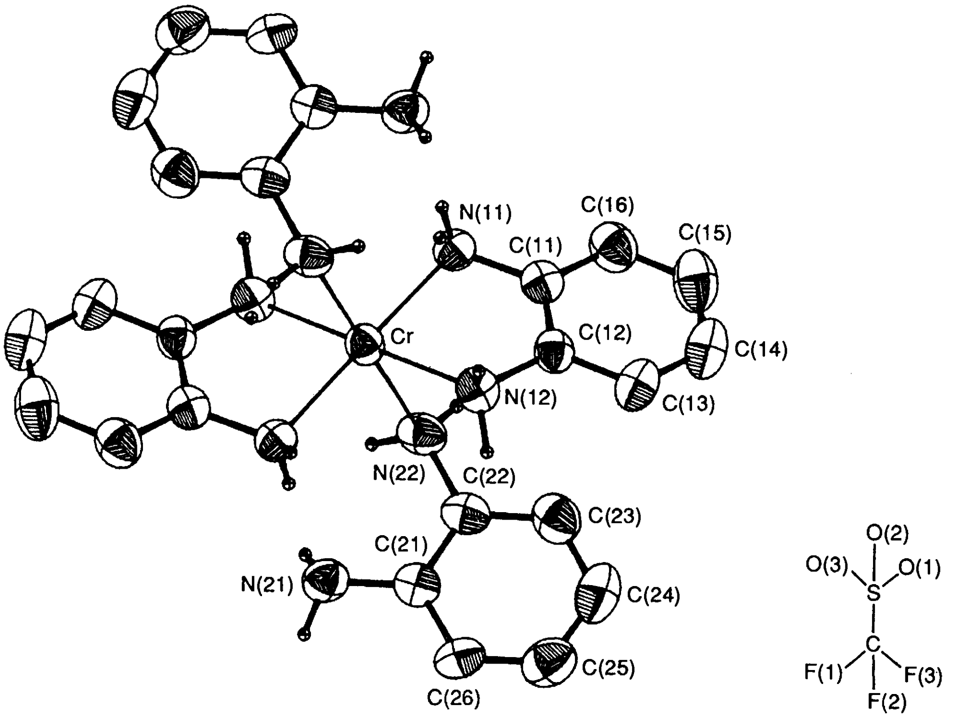

Fig. 3 Atom numbering scheme for $[Cr(opd)_4][CF_3SO_3]_2$

Table 4 Final atomic parameters for $[Cr(opd)_4][CF_3SO_3]_2$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr	0	0	0	C(15)	0.049 2(8)	0.229 2(3)	0.054 8(5)
S	0.026 0(2)	0.089 58(7)	0.418 2(1)	C(16)	−0.007 7(7)	0.177 5(3)	0.087 5(5)
F(1)	−0.125 7(6)	0.179 1(2)	0.364 3(3)	C(21)	0.370 6(6)	0.452 6(3)	0.221 1(4)
F(2)	−0.060 6(7)	0.117 1(2)	0.276 0(3)	C(22)	0.352 5(6)	0.415 0(3)	0.156 3(4)
F(3)	0.094 7(7)	0.177 6(2)	0.324 4(4)	C(23)	0.395 7(8)	0.355 8(3)	0.161 7(4)
O(1)	0.050 6(6)	0.123 8(2)	0.488 6(3)	C(24)	0.460 5(9)	0.334 6(3)	0.230 6(5)
O(2)	−0.102 3(5)	0.051 2(2)	0.419 6(3)	C(25)	0.483 6(8)	0.371 9(3)	0.293 7(5)
O(3)	0.155 9(5)	0.060 8(2)	0.386 8(3)	C(26)	0.435 8(7)	0.430 1(3)	0.289 2(4)
N(11)	−0.021 4(5)	0.066 9(2)	0.087 1(3)	H(11A)	0.031(5)	0.053(2)	0.127(3)
N(12)	0.160 0(5)	0.062 1(2)	−0.042 7(3)	H(11B)	−0.106(6)	0.066(2)	0.098(3)
N(21)	0.329 0(6)	0.512 9(2)	0.215 9(3)	H(12A)	0.176(8)	0.066(3)	−0.100(5)
N(22)	0.297 1(5)	0.439 2(2)	0.082 8(3)	H(12B)	0.234(6)	0.056(2)	−0.026(3)
C	−0.020 5(8)	0.143 6(3)	0.342 9(5)	H(21A)	0.259(6)	0.519(2)	0.192(3)
C(11)	0.033 1(6)	0.122 8(3)	0.056 0(4)	H(21B)	0.329(9)	0.529(3)	0.265(5)
C(12)	0.127 2(6)	0.120 4(2)	−0.008 4(4)	H(22A)	0.262(7)	0.410(3)	0.058(4)
C(13)	0.184 5(7)	0.172 4(3)	−0.040 3(4)	H(22B)	0.219(8)	0.466(3)	0.091(5)
C(14)	0.144 2(8)	0.226 1(3)	−0.008 3(5)				

Table 5 Selected bond distances (Å) and angles (°) for $[Cr(opd)_4]$-$[CF_3SO_3]_2$ with e.s.d.s in parentheses

Cr–N(11)	2.109(5)	N(11)–Cr–N(12)	80.2(2)
Cr–N(12)	2.128(5)	N(11)–Cr–N(22)	86.4(2)
Cr–N(22)	2.669(5)	N(12)–Cr–N(22)	87.1(2)
N(11)–C(11)	1.445(7)	C(15)–C(16)	1.382(10)
N(12)–C(12)	1.461(7)	C(16)–C(11)	1.388(9)
N(21)–C(21)	1.408(8)	C(21)–C(22)	1.389(8)
N(22)–C(22)	1.440(8)	C(22)–C(23)	1.388(9)
C(11)–C(12)	1.376(8)	C(23)–C(24)	1.384(11)
C(12)–C(13)	1.384(8)	C(24)–C(25)	1.368(11)
C(13)–C(14)	1.371(9)	C(25)–C(26)	1.379(10)
C(14)–C(15)	1.364(12)	C(26)–C(21)	1.384(9)
S–O(1)	1.429(5)	O(1)–S–O(2)	115.6(3)
S–O(2)	1.439(5)	O(1)–S–C	104.9(3)
S–O(3)	1.435(5)	S–C–F(1)	112.9(5)
S–C	1.805(8)	F(1)–C–F(2)	108.6(6)
F(1)–C	1.288(9)		
F(2)–C	1.323(9)		
F(3)–C	1.322(9)		

A 4 Å bond search revealed the following hydrogen bonds between all the oxygen atoms and the hydrogen atoms associated with the amine nitrogen atoms: O(1) ··· N(22) 3.068, O(2) ··· N(21) 3.176, O(2) ··· N(22) 3.063, O(2) ··· N(12) 2.986, O(3) ··· N(21) 3.076 and O(3) ··· N(11) 2.933 Å.

Final atomic parameters are given in Table 4 and bond lengths and angles in Table 5.

Additional material for both structures available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

A series of chromium(II) complexes containing one, two, four or six molecules of opd has been isolated (Table 1). With a particular anion, variation of the metal:ligand molar ratio over a considerable range did not affect the stoichiometry of the complex which separated except that $[Cr(opd)Cl_2]$ and $[Cr(opd)_6]Cl_2$ were obtained from chromium(II) chloride. Other than $[Cr(opd)_2(NCS)_2]$ and $[Cr(opd)Cl_2]$, the chro-

Table 6 Magnetic properties and diffuse reflectance spectra

	Magnetic properties				Reflectance spectra (cm^{-1})	
Complex	T/K	μ_{eff} [a]	θ [a]/°	$10^6\chi_L$ [b]	ν_2	ν_1
$[Cr(opd)Cl_2]$	293	3.77	280	134	24 000	11 000
	87	2.57			16 000	
$[Cr(opd)_2I_2]\cdot 1.5EtOH$	293	4.83	2	313	18 200	13 100(sh)
	87	4.78				
$[Cr(opd)_2(NCS)_2]$	293	4.19	130	236	17 400	12 050(sh)
	87	3.20			14 900(sh)	
$[Cr(opd)_4]Br_2$	293	4.84	3	418	17 700	12 500(sh)
	87	4.77			16 400(sh)	
$[Cr(opd)_4][CF_3SO_3]_2$	293	4.85	5	442	17 850	11 800(sh)
	87	4.73				
$[Cr(opd)_6]Cl_2$	293	4.81	8	569	17 550	12 500(sh)
	87	4.79				

[a] From $\mu_{eff} = 2.828 (\chi_{Cr}T)^{\frac{1}{2}}$. Curie–Weiss law taken as $\chi_{Cr}^{-1} \propto (T + \theta)$. [b] Diamagnetic correction ($cm^3\ mol^{-1}$).

Table 7 Infrared absorption maxima (cm^{-1})

		$\nu(C-NH_2)$		
Compound	$\nu(NH_2)$	Unco-ordinated NH_2	Co-ordinated NH_2	Bonding of opd
opd (solid) [a]	3385m, 3363m, 3178(vbr)	1276s		
$[Cr(opd)Cl_2]$ [b]	3256m, 3219s, 3198s, 3171m, 3100w, 3089w, 3050w	1280w	1234m, 1227(sh)	Bidentate?
$[Cr(opd)_2I_2]\cdot 1.5EtOH$ [c]	3212(sh), 3153s, 3100s	1267s [c]	1241m	Bidentate
$[Cr(opd)_2(NCS)_2]$ [d]	3419m, 3341m, 3258m, 3208m(br)	1290s	1223vw	Monodentate [e]
$[Cr(opd)_4]Br_2$	3396w, 3291m, 3190s(br), 3100	1278s	1231m	Monodentate
$[Cr(opd)_4][CF_3SO_3]_2$	3400s, 3373w, 3320m, 3303s, 3275m, 3250m, 3228s, 3204m, 3176m	Obscured by triflate bands		Mono- and bi-dentate [f]
$[Cr(opd)_6]Cl_2$	3382m, 3357s, 3151s(br), 3031w(br)	1278s	1244w, 1236w	Mono- and bi-dentate
$[Ni(opd)_6]Cl_2$ [g]	3399m, 3377s, 3305m(br), 3141s(vbr), 3089m, 3033s(vbr)	1275s	1248w, 1235m	Mono- and bi-dentate

[a] opd also has a very weak band at 1247 cm^{-1}. [b] ν(Cr–Cl) at 310 cm^{-1}. [c] ν(OH) at 3413m(vbr) cm^{-1}; the band at 1267 cm^{-1} is due to δ(OH) and one at 1288 cm^{-1} is too weak to be due to an unco-ordinated CN stretching vibration. [d] Bands indicative of isothiocyanato ligands at: 2104vs, ν(CN); 940vw, 2 × δ(NCS); 811w, ν(CS); 470m, δ(NCS) and 340 cm^{-1}, ν(Cr–NCS). [e] Confirmed by structure determination (Fig. 1). [f] Confirmed by structure determination (Fig. 3). [g] More correctly formulated as $[Ni(opd)_4]Cl_2\cdot 2opd$.[7]

mium(II) complexes are high spin with effective magnetic moments (Table 6) close to the spin-only value (4.90) which show little variation with temperature. The low magnetic moments of the thiocyanato- and chloro-complexes at room temperature, which decrease still further as the temperature is lowered, indicate antiferromagnetic behaviour and therefore polymeric structures. The crystal-structure determinations show that $[Cr(opd)_2(NCS)_2]$ has a thiocyanato-bridged structure (Fig. 2) whereas $[Cr(opd)_4][CF_3SO_3]_2$, representative of the complexes with simple magnetic behaviour, is mononuclear (Fig. 3). Single crystals of $[Cr(opd)Cl_2]$ could not be obtained, but it is presumably a chloride-bridged polymer. The diffuse reflectance spectra of all complexes are typical[14] of high-spin, distorted six-co-ordinate, chromium(II) complexes.

o-Phenylenediamine can function as a mono- or a bi-dentate ligand, and the nature of its co-ordination has been inferred from the positions of the IR absorption bands in the NH and CN stretching regions.[3–6] In the spectrum of unco-ordinated opd the CN stretching frequency is at 1276 cm^{-1}, and it has been found that with aromatic amines the CN stretching frequency is lowered by 20–50 cm^{-1} on co-ordination. In all known opd complexes a strong CN absorption is found in the 1260–1230 cm^{-1} region; for example $[Ni(opd)_3][NO_3]_2$, which from electronic spectroscopy and conductance measurements is a tris(chelate) complex, has one band at 1255 cm^{-1}. However, $[Ni(opd)_4]Cl_2$, which must contain ligands with co-ordinated and unco-ordinated NH_2 groups, has an additional absorption at 1282 cm^{-1}, and $[Ni(opd)_6]Cl_2$, now known[7] to be $[Ni(opd)_4]Cl_2\cdot 2opd$ with mono-, bi-dentate and lattice diamine, has an additional absorption at 1275 cm^{-1}. Thus a strong band near 1280 cm^{-1} indicates unco-ordinated NH_2 groups and one in the 1260–1230 cm^{-1} region co-ordinated groups. The position of the NH stretching absorptions is also diagnostic: a band above 3350 cm^{-1} is indicative of unco-ordinated NH_2 groups whereas co-ordinated NH_2 groups show no strong bands above 3330 cm^{-1}. From these criteria the presence of bi- and/or mono-dentate amine in the chromium(II) complexes has been inferred (Table 7). The predictions from the IR spectra of the denticity of the amine ligands in $[Cr(opd)_4][CF_3SO_3]_2$ and $[Cr(opd)_2(NCS)_2]$ have been borne out by the crystal-structure determinations.

The $t_{2g}^3e_g^1$ configuration of high-spin chromium(II) is expected to lead to Jahn–Teller distortion of a CrN_6 chromophore. Although there is no detailed structural information, this effect is apparent in the solid-state electronic spectra of, for example, $[Cr(en)_3]Cl_2$ and $[Cr(dien)_2]Cl_2$, where en is ethylenediamine and dien is diethylenetriamine.[14] No tris(bidentate opd) complexes of chromium(II) have been isolated for direct comparison, but in $[Cr(opd)_4]^{2+}$ there are two *trans*-monodentate opd ligands, Cr–N 2.669 Å, and two bidentate opd ligands, mean Cr–N 2.118 Å (Fig. 3 and Table 5). This is the first crystallographic demonstration of distortion in a chromium(II) complex with a CrN_6 co-ordination sphere. An analogous cation structure was proposed[3] for the nickel(II) complexes $[Ni(opd)_4]X_2$, where X = Cl or Br, based on evidence from IR and diffuse reflectance spectra, and found by an X-ray crystal-structure determination[7] in $[Ni(opd)_6]Cl_2$. The four equatorial nickel–nitrogen ($Ni-N_{eq}$) distances in $[Ni(opd)_4]^{2+}$ are 2.102 Å and the two axial distances ($Ni-N_{ax}$)

are 2.267 Å (Ni–N$_{ax}$/Ni–N$_{eq}$ = 1.08). The longer axial bonds are ascribed to steric crowding about the metal atom since with less bulky ligands, *e.g.* ammonia, nickel(II) ($t_{2g}^6e_g^2$ configuration) forms NiN_6 complexes with Ni–N bonds of essentially equal length.[7] The distortion of the co-ordination sphere in the chromium(II) complex is much greater (Cr–N$_{ax}$/Cr–N$_{eq}$ = 1.26) presumably due to combined steric and Jahn–Teller effects.

The *trans*-planar units of $[Cr(opd)_2(NCS)_2]$ are arranged in the lattice so that the S atoms of two adjacent units 2.972 Å distant complete the co-ordination shell and produce a thiocyanato-bridged infinite-chain polymer. This structure contrasts with that of $[Cr(tu)_2(NCS)_2]$, where tu is thiourea, which stacks so that the chromium atoms of adjacent units interact weakly.[15] The Cr–N(amine) distance is similar to the short Cr–N distances in $[Cr(opd)_4]^{2+}$, and the Cr–NCS distance is close to that in $[Cr(tu)_2(NCS)_2]$ (2.026 Å). As might be expected, the C–N bond distances to the co-ordinated amino groups are longer than those to the unco-ordinated groups (*ca.* 1.45 and 1.41 Å respectively), and the other internal dimensions of the opd ligands are similar in the thiocyanato-complex and the triflate.

Since $[Cr(NH_3)_6]^{2+}$ readily loses one ammonia molecule as does $[Cr(en)_3]^{2+}$ one ethylenediamine (en) molecule,[14] the isolation of $[Cr(opd)_6]Cl_2$ apparently containing solely monodentate diamine was surprising. However, the infrared spectrum of $[Cr(opd)_6]Cl_2$ resembles that of $[Ni(opd)_6]Cl_2$ first thought to contain six monodentate opd molecules from its spectroscopic and thermal behaviour but now known to be $[Ni(opd)_4]Cl_2{\cdot}2opd$. This model was rejected by Marks *et al.*,[3] largely because of differences in the thermal behaviour of a sample of $[Ni(opd)_6]Cl_2$ and one of $[Ni(opd)_4]Br_2$ mixed with free opd, which showed a melting endotherm for the opd at 108 °C. The X-ray crystal structure showed the lattice opd to be held in an extensive hydrogen-bonded network with the $[Ni(opd)_4]^{2+}$ and chloride ions so that the loss of opd took place at a higher temperature than the melting endotherm. It would seem that $[Cr(opd)_6]Cl_2$ should also be formulated as $[Cr(opd)_4]Cl_2{\cdot}2opd$, with a cation of the same structure as in the triflate, and two *o*-phenylenediamine molecules in the lattice. The reflectance spectra of the two complexes are similar, but we have not been able to obtain single crystals of $[Cr(opd)_6]Cl_2$ for X-ray investigation.

The iodide $[Cr(opd)_2I_2]{\cdot}1.5EtOH$ is believed to contain only bidentate diamine because there is no sharp NH absorption near 3300 cm^{-1} and only a weak band at 1288 cm^{-1}. It is possible that iodide is co-ordinated but as it is such a weak ligand the co-ordination of ethanol cannot be excluded. On the other hand the bromide is believed to contain solely monodentate diamine with axial bromides completing a *trans* distorted-octahedral arrangement. This is because the unbonded amine group C–N stretching frequency is relatively intense as for $[Cr(opd)_2(NCS)_2]$, and there is a band at 270 cm^{-1} assignable to a Cr–Br stretching frequency.[16]

After the attempts described above to prepare $[CrL^1]$ by template reactions failed, we found that red crystals analysing as $CrL^1{\cdot}0.5C_6H_5Me$ could be isolated from the reaction between anhydrous chromium(II) acetate and Li_2L^1. It seemed probable that Cr^{2+} like Mo^{2+} is too large to fit into the tetraazaannulene ring, and might form a dimer $Cr_2L^1{}_2$ with a metal–metal bond but no bridging ligands analogous to the known $[Mo_2L^1{}_2]$[17] During the course of our work the preparation of $[CrL^1]$ by reaction between $[\{Li_2Cr(Me_4)_4(thf)_2\}_2]$ and H_2L^1, or $[Cr(thf)_2Cl_2]$ and Li_2L^1 (thf = tetrahydrofuran), was reported,[18] and the compound is an unbridged Cr–Cr dimer. This explains our failure to obtain a chromium(II) macrocycle by a template procedure.

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