

**SYNTHESES AND CHARACTERIZATION OF COPPER(II) AND COBALT(II) COMPLEXES WITH TRIS[2-(BENZYLAMINO)ETHYL]AMINE**

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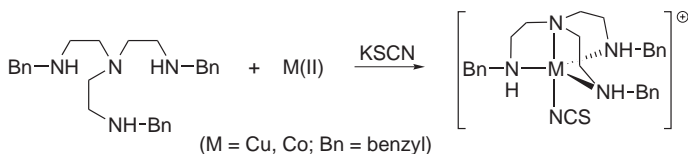
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Two mononuclear complexes [Cu(NCS)(trenb)]ClO<sub>4</sub> (**1**) and [Co(NCS)(trenb)]Cl·H<sub>2</sub>O (**2**), where trenb is tris[2-(benzylamino)ethyl]amine, were prepared and characterized by elemental analysis, IR, electronic and EPR spectra. Their crystal structures were determined by X-ray diffraction. Complexes **1** and **2** are both five-coordinated with their metal centers in the distorted trigonal-bipyramidal environment. Each metal(II) ion coordinates with the tetradentate trenb, and one isothiocyanate anion. The two complexes are not isostructural as there are also a chloride and a water molecule in the asymmetric unit of **2**. Besides balancing the charge, the chlorides are also involved in intramolecular and intermolecular hydrogen bonds with the secondary amine groups, resulting in a one-dimensional chain structure. UV-VIS spectrum and EPR measurement for **1** have unambiguously confirmed that the five-coordinated structure is retained in solution, even in the donating solvent such as DMF. **Keywords:** Copper(II) complexes; Cobalt(II) complexes; Crystal structure determination; Tren derivative; Tripodal ligands; X-Ray diffraction.

Great interest has been focused on the metal complexes of tripodal ligands, especially to model functions or spectroscopic features of metalloenzymes<sup>1</sup> and to study the factors that cause various distortions from regular stereochemistry<sup>2</sup>. Some of them have been found to possess special features, such as reversible binding of dioxygen<sup>3</sup>, which threw some light on the fundamental step in metalloenzyme redox reactions. The ideas of utilizing them in the syntheses of highly symmetrical molecular cages, which are potentially suitable for molecular recognition, are also considered<sup>4</sup>. Among the tripodal ligands, tren (tris(2-aminoethyl)amine) attracted much attention, partly because of its ability to form uncommon five-coordinated complexes

with divalent metal ions<sup>5</sup>. However, investigation of the complexes of its derivatives, in particular the investigation of the steric hindrance induced by the modification, was relatively scarce<sup>6</sup>, being mainly limited to less bulky groups such as methyl<sup>3d,7</sup>. Thus, we chose larger substituent groups to gain further insight of complexes of the tren derivatives.

Herein, we report the syntheses, as well as spectroscopic and structural characterization of Cu(II) and Co(II) complexes with a tripodal ligand, tris[2-(benzylamino)ethyl]amine (Scheme 1).



SCHEME 1

## RESULTS AND DISCUSSION

### Spectra

The IR spectra of the title complexes show sharp vibration bands due to the  $\nu(\text{CN})$  stretching. In complex **1**, the strong band lies at  $2106\text{ cm}^{-1}$  and it appears at  $2059\text{ cm}^{-1}$  in complex **2**. Other noticeable bands appear at  $3288$  and  $3249\text{ cm}^{-1}$  in **1** and  $3238\text{ cm}^{-1}$  in **2**, which belong to the  $\nu(\text{NH})$ . The bands at  $1086$  and  $622\text{ cm}^{-1}$  are assigned to the perchlorate ion in complex **1**.

Featureless EPR spectra were observed for polycrystalline samples of **1** at room temperature and at 100 K. In DMF solution, an isotropic spectrum containing four hyperfine lines is observed at room temperature, while the spectrum at 100 K has an axial symmetry, exhibiting four hyperfine peaks in the perpendicular region with  $g_{\parallel} = 1.993$ ,  $g_{\perp} = 2.195$ ,  $g_{\text{iso}} = 2.144$ ,  $A_{\text{iso}} = 68.2\text{ G}$ ,  $A_{\perp} = 113.3\text{ G}$ ,  $A_{\parallel} = 22.0\text{ G}$  ( $1\text{ G} = 10^{-4}\text{ T}$ ). The data mostly fall in the region reported<sup>7a</sup> except  $A_{\parallel}$ , which varies significantly in the copper(II) complexes of tren and its derivatives, mainly depending on their spin-orbit coupling constants. The fact  $g_{\perp} > g_{\parallel}$  confirms a distorted trigonal-bipyramidal stereochemistry with a  $(d_{z^2})^1$  ground state in complex **1**<sup>8</sup>. The  $g_{\parallel} < 2.0$  may result from the “reversed axial” pattern that copper(II) complexes in the trigonal-bipyramidal (TBP) geometry with tripodal ligands normally display in the frozen-solution EPR spectra<sup>8b,9</sup>.

The electronic spectra of complexes **1** and **2**, measured in DMF solution, are reported in Table I. The spectrum of **1** shows a sharp band at 850 nm and an asymmetric high-energy shoulder with the maximum at 676 nm, characteristic of a distorted trigonal-bipyramidal  $\text{CuN}_5$  chromophore<sup>10</sup>. The two transitions are assigned as  $(d_{xy}, d_{x^2-y^2}) \rightarrow d_{z^2}$  (lower energy) and  $(d_{yz}, d_{xz}) \rightarrow d_{z^2}$ . Comparing to the copper(II) complexes of tren and  $\text{trenMe}_6$ , the d-d bands both move to the higher energy as the bulkier amines inhibit the approach of adjacent molecules and decrease the axial interaction, resulting in stronger in-plane bonding<sup>7a</sup>. The two bands of **1** are obviously more intensive than those of the tren complex, but a little distinction in intensity is found between **1** and the  $\text{trenR}_6$  (R = Me, Et) complexes.

The spectral features of **2** are difficult to fully explain, since the spectra of five-coordinated cobalt(II) complexes considerably vary depending on the nature of the distortion<sup>11</sup>. In complex **2**, there are broad bands at 606 and 492 nm, associated with the d-d transitions, with a shoulder at a lower energy (756 nm). The results are parallel to the reported examples<sup>12</sup> of the trigonal-bipyramidal geometry of cobalt(II). The remaining band maxima near or below 300 nm are due to the intraligand transitions as follows from similarities with the absorbance of the "free" ligand.

### Structure Description

The perspective drawings for complexes are shown in Figs 1 and 2. Selected bond lengths and bond angles are listed in Tables II and III. The structure of **1** consists of  $[\text{Cu}(\text{NCS})(\text{trenb})]^+$  cation and  $\text{ClO}_4^-$  anion. In the cation, the copper(II) ion is in a distorted trigonal-bipyramidal geometry with three secondary amine groups of the trenb ligand forming the equatorial plane

TABLE I  
Summary of electronic spectral data<sup>a</sup>

Compound	$\lambda_{\text{max}}$ , nm ( $\epsilon$ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )
Trenb·3HCl	281 (1500), 267 (6250)
<b>1</b>	850 (408), 676 (200), 287 (6240), 262 (4500)
<b>2</b>	756 (27), 606 (116), 492 (103), 306 (310), 264 (803)

<sup>a</sup> Spectra recorded in DMF.

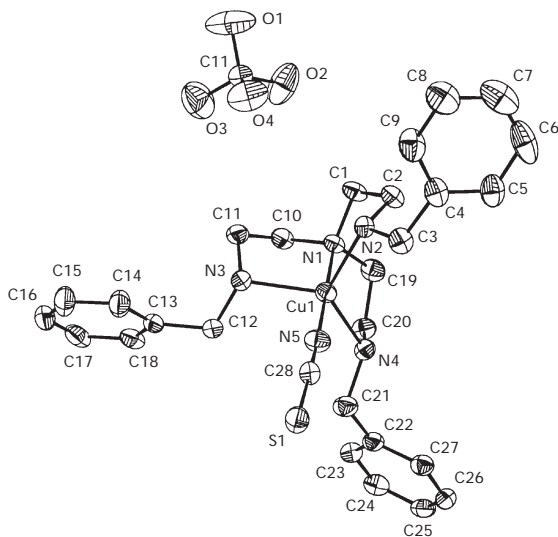


FIG. 1

View of complex  $[\text{Cu}(\text{NCS})(\text{trenb})]\text{ClO}_4$  (**1**) showing the numbering scheme at the 30% probability level with the H atoms omitted for clarity

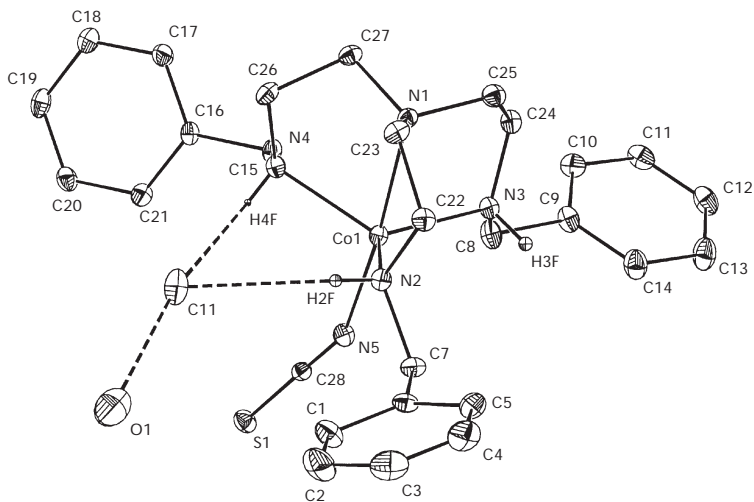


FIG. 2

An ORTEP view of  $[\text{Co}(\text{NCS})(\text{trenb})]\text{Cl}\cdot\text{H}_2\text{O}$  (**2**) showing the numbering scheme. The thermal ellipsoids are at the 10% probability level with the H atoms omitted for clarity

and with the tertiary amine and  $\text{NCS}^-$  in the apical positions. The square-pyramidal component of structural index  $\tau$  is 0.88 (for ideal square-pyramidal and trigonal-bipyramidal geometries the values are zero and unity, respectively)<sup>13</sup>. The axis N(1)–Cu–N(5) (angle of  $178.96(8)^\circ$ ) is roughly perpendicular ( $90.76^\circ$ ) to the equatorial plane. The interchelate bond angles, such as N(1)–Cu–N(2) ( $84.15(7)^\circ$ ), agrees with that of  $84.1^\circ$

TABLE II  
Selected bond lengths (in Å) and bond angles (in  $^\circ$ ) for **1**

Cu1–N5	1.928(2)	Cu1–N3	2.152(2)
Cu1–N2	2.113(2)	Cu1–N1	2.037(2)
Cu1–N4	2.107(2)	S1–C28	1.618(3)
N5–C28	1.169(3)		
N5–Cu1–N2	96.89(8)	N5–Cu1–N3	95.83(9)
N2–Cu1–N3	113.78(8)	N5–Cu1–N4	94.44(9)
N2–Cu1–N4	125.93(8)	N3–Cu1–N4	117.34(8)
N5–Cu1–N1	178.96(8)	N2–Cu1–N1	84.15(7)
N3–Cu1–N1	83.75(8)	N4–Cu1–N1	84.92(8)
C28–N5–Cu1	175.5(2)	N5–C28–S1	178.4(2)

TABLE III  
Selected bond lengths (in Å) and bond angles (in  $^\circ$ ) for **2**

Co1–N5	2.027(5)	Co1–N3	2.095(4)
Co1–N2	2.087(5)	Co1–N1	2.214(5)
Co1–N4	2.103(5)	S1–C28	1.613(6)
N5–C28	1.162(7)		
N5–Co1–N2	102.2(2)	N5–Co1–N3	101.4(2)
N2–Co1–N3	117.6(2)	N5–Co1–N4	94.4(2)
N2–Co1–N4	115.8(2)	N3–Co1–N4	118.9(2)
N5–Co1–N1	174.9(2)	N2–Co1–N1	80.5(2)
N3–Co1–N1	80.9(2)	N4–Co1–N1	80.5(2)
C28–N5–Co1	154.5(5)	N5–C28–S1	179.2(5)

in [Cu(NCS)(tren)](SCN)<sup>14</sup>. The three out-of-plane chelate bite angles imposed by the ligand lead to the fact that the copper(II) ion is displayed by 0.21 Å below the equatorial plane towards the NCS<sup>-</sup>. The equatorial plane is not strictly triangular: one of the N(2)–Cu–N(4) angle of 125.93(8)° is significantly larger than the other two and the distance of the Cu–N(3) bond (2.152(2) Å) opposite to the angle is longer than the other two Cu–N bonds. The Cu–N(tertiary amine) distance (2.037(2) Å) is the shortest of the four nitrogen atoms from trenb ligand and consistent with the literature<sup>3e,5,7b,10a,14</sup>. The axial compression was commonly considered as a result of its d<sup>9</sup> configuration in this stereochemistry<sup>10a</sup>. The Cu–N(thiocyanate) bond of 1.928(2) Å was even shorter due to the π-bonding component and similar to that in [Cu(NCS)(tren)](SCN)<sup>14</sup>.

Cation in complex **2** is similar to that appearing in **1**, although the two complexes are not isostructural. The cobalt(II) ion is also in a distorted trigonal-bipyramidal geometry with its coordination environment in coincidence with that of **1**. The pseudo-three-fold axis is aligned with N(1)–Co–N(5) (174.9(2)°) and is almost perpendicular (89.84°) to the equatorial plane containing three amine nitrogen atoms, which make almost an equilateral triangle. The cobalt(II) ion is about 0.34 Å out of the plane towards the NCS<sup>-</sup> and the deviation is somewhat larger than that of the copper(II) in complex **1**. However, the Co–N bond lengths differ greatly from those in **1**: the Co–N(tertiary amine) distance (2.214(5) Å) is now dramatically longer than the other three nitrogen atoms from the trenb ligand (2.087(5)–2.103(5) Å), though still similar to the values found in literature<sup>15</sup>. The other parameters are common.

The angle M–N–C(thiocyanate) (M means metal ion) differs greatly in the two complexes. The Co–N–C (154.6°) deviates markedly from the pseudo-three-fold axis than the angle Cu–N–C (175.5°) does, and the values are different from those found in the literature, such as 163.3° in [Cu(NCS)(tren)](SCN)<sup>14</sup> and 163.4 and 156.3° in octahedral [Ni(NCS)<sub>2</sub>(tren)]<sup>16</sup>. The situation is common, as the isothiocyanate ion can flexibly choose any appropriate coordinating direction after the tripodal ligand occupy the apex and the equatorial plane of the complex. Thus the steric hindrance may be determinant. In complex **2**, the strain of Co–N–C(isothiocyanate) bonds was caused by the benzyl groups, which appears alleviative in complex **1**.

There are also a chloride and a water molecule in the crystal unit of **2**. Besides balancing the charge, the chloride also weakly interacts with three hydrogen atoms from secondary amine groups. It is clear that chloride interacts with H(2F) and H(4F) atom (the distances are 2.639 and 2.713 Å, respectively) but not H(3F) (about 6.14 Å), which always interacts with the

chloride in the adjacent molecule (2.488 Å), as Fig. 3 shows. Thus, the crystal units can be considered as being connected *via* weak interactions between chlorides and hydrogen atoms to give a one-dimensional chain. The water molecule interacts with the chloride with the Cl...O distance of 2.473 Å. The unusual short Cl...O bond may owe to the effect of the very strong hydrogen bonds, which normally shorten the relative distance sharply<sup>17</sup>. However, comparable data concerning Cl...H-O hydrogen bonds are rare due to the heavy effects of the thermal vibration artifacts<sup>17b</sup>. Though direct evidence is unavailable, the hydrogen of the water may be presumed to delocalize to some extent and be in an equilibrium state with chloride and oxygen. Thus the water molecule is also admitted as a member of the one-dimensional chain.

## EXPERIMENTAL

### General Comments

All the reagents were commercially available and were used without further purification. <sup>1</sup>H NMR spectra were recorded on a Bruker DMX-500 spectrometer in DMSO-*d*<sup>6</sup> solutions at 298 K. Chemical shifts ( $\delta$ , ppm) are given relative to internal tetramethylsilane. IR spectra (wavenumbers in  $\text{cm}^{-1}$ ) were measured on a Bruker Vector-22 spectrometer (range 400–4 000  $\text{cm}^{-1}$ ). Electronic spectra were obtained on a Shimadzu UV-3100 UV-VIS-NIR recording spectrophotometer ( $\lambda_{\text{max}}$  in nm,  $\epsilon$  in  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) in the range 200–900 nm. Microanalyses of C, H and N were carried out with a VARIO ELIII elemental analyzer. EPR studies were performed with a Bruker ER200D-SRC spectrometer at X-band (9.46 GHz).

**Safety note!** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of the material should be prepared and handled with extreme care.

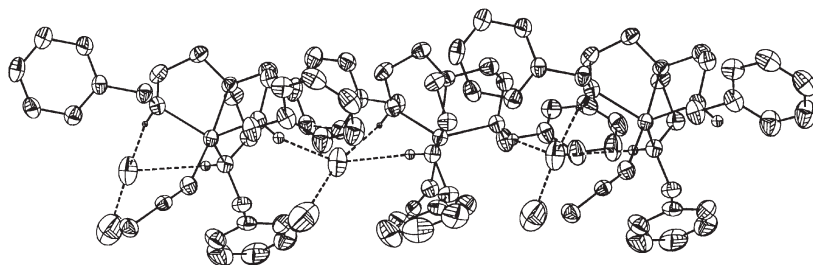


FIG. 3

Molecular packing in structure of  $[\text{Co}(\text{NCS})(\text{trenb})]\text{Cl}\cdot\text{H}_2\text{O}$  (**2**). The figure shows the weak interactions N–H...Cl resulting in a one-dimensional chain

## Syntheses

## Tris[2-(benzylamino)ethyl]amine Trihydrochloride (trenb-3HCl)

To a stirred solution of 15.5 ml of 98% benzaldehyde (0.15 mol) in ethanol (25 ml) was added tris(2-aminoethyl)amine (7.6 ml, 0.05 mol). After refluxing for 4 h, potassium borohydride (5.5 g) in a morsel of water was added over 15 min. The original yellow color slowly faded. When the evolution of the gas slackened, the solution was cooled and then acidified with conc. hydrochloric acid to pH 3. The amount of the white precipitate reduced by adding 4 M KOH solution until pH about 9. After filtration, the solution was extracted with  $3 \times 50$  ml chloroform and the organic phase was dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to dryness. The residual oil was dissolved in 50 ml ethanol and pH of the solution was adjusted by concentrated hydrochloric acid to strong acidic. A soft white powder was obtained. The solid was washed with ethanol and then dried *in vacuo*. Yield 10.5 g (40%). For  $\text{C}_{27}\text{H}_{39}\text{Cl}_3\text{N}_4$  (526.0) calculated: 61.43% C, 7.45% H, 10.72 % N; found: 61.65% C, 7.47% H, 10.65% N. IR (KBr):  $\nu$ (hydrochloride) 2500–2900 br, 1456 s, 1434 m, 1371 m, 1021 m composite, 744 s, 694 s.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ): 9.54 apparent s, 6 H ( $-\text{NH}_2^+$ ); 7.42 apparent t, 9 H (Ar-H); 7.65 apparent t, 6 H (Ar-H); 4.22 apparent s, 6 H ( $\text{ArCH}_2-$ ); 3.12 apparent s, 6 H ( $-\text{NH}_2^+\text{CH}_2-$ ); 2.80 apparent t, 6 H ( $>\text{NCH}_2-$ ).

[Cu(NCS)(trenb)]ClO<sub>4</sub> (1)

A methanolic solution (10 ml) of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.074 g, 0.20 mmol) was added dropwise to a stirred solution of trenb-3HCl (0.083 g, 0.16 mmol) in methanol (40 ml). Then the mixture was made strongly alkaline with 4 M aqueous NaOH (0.30 ml). Finally, KSCN (0.038 g, 0.40 mmol) dissolved in a small volume of water was added slowly. The clear green-blue solution was refluxed for 3 h, filtered to remove a small quantity of a precipitate and left undisturbed at room temperature. After a few months, crystals suitable for X-ray analysis were filtered off, washed several times with water-ethanol (1 : 1, v/v) and air-dried. Yield 0.026 g (25%). The analysis for the bulk material was consistent with the formula proposed. For  $\text{C}_{28}\text{H}_{36}\text{ClCuN}_5\text{O}_4\text{S}$  (637.7) calculated: 52.74% C, 5.69% H, 10.98% N; found: 52.46% C, 5.37% H, 10.71% N. IR (KBr):  $\nu$ (NH) 3288 m, 3249 m, 2923 m;  $\nu$ (CN) 2106 s, 1455 m, 1343 w, 1203 w, 1086 br, 988 s, 830 w, 746 s, 705 s, 622 m.

[Co(NCS)(trenb)]Cl·H<sub>2</sub>O (2)

A methanolic solution (10 ml) of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.074 g, 0.20 mmol) was added dropwise to a stirred solution of trenb-3HCl (0.083 g, 0.16 mmol) in methanol (40 ml). The dark blue solution darkened after a solution of KSCN (0.038 g, 0.40 mmol) in a small volume of water was slowly added. A mass of green crystals was grown from the rosy solution only after evaporation of some solvent. The crystalline product was collected by filtration, washed with water-ethanol (1 : 1, v/v) and dried in the air. Yield 0.024 g (21%). The analysis of the bulk material was consistent with the formula proposed. For  $\text{C}_{28}\text{H}_{38}\text{ClCoN}_5\text{SO}$  (587.1) calculated: 57.28% C, 6.52% H, 11.93% N; found: 57.34% C, 6.53% H, 11.78% N. IR (KBr): 3418 m;  $\nu$ (NH) 3238 w, 3079 m, 2947 w;  $\nu$ (CN) 2060 s, 1495 m, 1454 m, 1345 m, 1207 w, 1077 m, 1044 w, 1003 m, 960 w, 851 w, 742 m, 702 s, 625 m.



*X-Ray Crystallography*

Single crystals were mounted on a glass fiber. All measurements were made with a Rigaku RAXIS-IV image plate area detector with graphite-monochromatized MoK $\alpha$  radiation. The data were collected at the temperatures listed in Table IV and corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle

TABLE IV  
Crystal data and structure refinement for **1** and **2**

Compound	<b>1</b>	<b>2</b>
Molecular formula	C <sub>28</sub> H <sub>36</sub> ClCuN <sub>5</sub> O <sub>4</sub> S	C <sub>28</sub> H <sub>36</sub> ClCoN <sub>5</sub> OS
Formula weight	637.67	585.06
Crystal color and habit	blue, plate	dark red, prism
Crystal dimension, mm	0.22 × 0.20 × 0.12	0.28 × 0.20 × 0.20
System space group	monoclinic, <i>P2</i> <sub>1</sub> / <i>c</i>	orthorhombic, <i>Pbac</i>
<i>T</i> , K	294(2)	291(2)
<i>a</i> , Å; $\alpha$ , °	11.3134(15); 90	14.729(3); 90
<i>b</i> , Å; $\beta$ , °	29.246(4); 113.379(3)	16.039(3); 90
<i>c</i> , Å; $\gamma$ , °	9.8149(13); 90	25.214(5); 90
<i>V</i> , Å <sup>3</sup> , <i>Z</i>	2980.8(7); 4	5956.2(20); 8
<i>D</i> <sub>c</sub> , g cm <sup>-3</sup>	1.421	1.305
<i>F</i> (000); $\mu$ (MoK $\alpha$ ), mm <sup>-1</sup>	1332; 0.934	2456; 0.765
$\theta$ range, °	1.0–27.5	2.0–25.2
<i>hkl</i> range	–12/14, –37/36, –12/12	–19/19, –20/0, –32/32
No. of unique diffractions	6840	5964
No. of observed diffractions <sup>a</sup>	3463	3213
No. of parameters	358	347
<i>R</i> , <i>wR</i> for observed diffractions <sup>b</sup> , %	4.84, 13.53	7.93, 14.70
<i>R</i> , <i>wR</i> for all data <sup>b</sup> , %	10.77, 16.40	21.82, 18.49
<i>R</i> <sub>int</sub>	0.0529	0.0824
GOF for all data <sup>c</sup>	0.823	1.099
Residual electron density, e Å <sup>-3</sup>	0.816/–0.505	0.289/–0.564

<sup>a</sup> Diffractions with  $I > 2\sigma(I)$ . <sup>b</sup>  $R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ ,  $wR(F^2) = \frac{[\sum (w(F_o^2 - F_c^2))^2 / (\sum w(F_o^2))^2]^{1/2}}$ .  
<sup>c</sup> GOF =  $[\sum (w(F_o^2 - F_c^2))^2 / (N_{\text{diffrs}} - N_{\text{params}})]^{1/2}$ .

of full-matrix least-squares refinement was based on observed reflections ( $I > 2.00\sigma(I)$ ) and variable parameters. All calculations were performed using SHELX97 software package<sup>18</sup>. Abbreviated crystal data are summarized in Table IV. CCDC 183909 (for structure **1**) and CCDC 183908 (for structure **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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