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A new one-dimensional system starting from a trinuclear copper(II) complex and selenocyanate as bridging ligand. Comparison with the thiocyanate analogue

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A new copper(II) bridging-selenocyanate complex has been synthesized starting from the known trinuclear copper(II) complex, $[\{Cu(tmen)\}_2\{\mu\text{-}Cu(pba)\}][ClO_4]_2$ [tmen = *N,N,N′,N′*-tetramethylethane-1,2-diamine and H_4pba = *N,N′*-propane-1,3-diylbis(oxamic acid)]. The reaction of an aqueous solution of this complex with KSeCN gave good crystals of the new one-dimensional compound in which two selenocyanate ligands are linked to each terminal copper(II) ion. Both these ligands are weakly Se-coupled to the central copper(II) atom of another trinuclear entity giving a pseudo one(two)-dimensional structure. The magnetic behaviour was recorded between 300 and 4 K, showing strong intramolecular antiferromagnetic coupling ($J = -356$ cm^{-1}, $g_C = 2.20$ and $g_T = 2.21$; C = central, T = terminal Cu atom) and very weak intermolecular ferromagnetic coupling.

In a previous study[1] we reported a new one-dimensional system made by treating the known[2] trinuclear copper(II) complex $[\{Cu(tmen)\}_2\{\mu\text{-}Cu(pba)\}][ClO_4]_2$ with NaSCN [tmen = *N,N,N′,N′*-tetramethylethane-1,2-diamine and H_4pba = *N,N′*-propane-1,3-diylbis(oxamic acid)]. This new complex is a chain of trinuclear entities with two N-thiocyanato terminal ligands linked by the sulfur atom to the central copper(II) atom of another trinuclear entity. The interest in it was the possibility of ferromagnetic interactions between the trinuclear entities, bearing in mind the known tendency of thiocyanate anion to give ferromagnetic coupling when it bridges in end-to-end mode. This tendency is very clear for nickel(II) [3–10] complexes but less pronounced for copper(II) due to the low number of complexes reported.[11] Consequently the behaviour of this system could be the opposite to that reported by Drillon *et al.*,[12,13] where copper(II) trimers were coupled in an antiferromagnetic arrangement to give a new ferrimagnetic model: $A_2Cu_3(PO_4)_4$ (A = Ca or Sr). As indicated in our previous work,[1] the same reaction with NaN_3 allows us to prepare only a dinuclear copper(II) complex, already reported by Kahn and co-workers,[14] and with NaNCO the reaction did not take place. Working with KSeCN we were able to prepare a new complex, very similar to the thiocyanato analogue, in which the only difference lies in the distance between the selenium atom of the terminal selenocyanate ligand and the copper(II) central atom of the neighbouring entity, compared with the distance from the sulfur atom to a copper(II) ion: Se···Cu (central) 3.06 and 3.465; S···Cu (central) 3.014 and 3.617 Å. This paper describes the first selenocyanato-bridged one-dimensional complex prepared from trinuclear copper(II) entities with the aim of studying the co-ordination and magnetic properties of the end-to-end selenocyanato bridges.

Experimental

Synthesis

The salt $Na_2[Cu(pba)]\cdot 6H_2O$ was synthesized as previously described.[15]

$[\{Cu(tmen)(SeCN)\}_2\{\mu\text{-}Cu(pba)\}]$ 1. An ethanolic solution of *N,N,N′,N′*-tetramethylethane-1,2-diamine (0.48 g, 4.14 mmol) was added to a stirred solution of copper(II) nitrate hexahydrate (1 g, 4.14 mmol) in ethanol (50 cm^3). Then solutions of $Na_2[Cu(pba)]\cdot 6H_2O$ (0.89 g, 2.07 mmol) in water (50 cm^3) and KSeCN (0.3 g, 2.07 mmol) in water (5 cm^3) were added consecutively. The resultant blue solution was filtered to remove any impurity and left to evaporate slowly at room temperature. Blue monocrystals suitable for X-ray determination were collected after 2 weeks (yield *ca.* 60%) (Found: C, 28.5; H, 4.9; N, 12.6. Calc. for $C_{21}H_{42}Cu_3N_8O_8Se_2$: C, 28.6; H, 4.8; N, 12.7%).

Spectral and magnetic measurements

Infrared spectra were recorded on a Nicolet 520 FT-IR spectrometer. Magnetic susceptibility measurements in the range 300–4 K were made on polycrystalline samples with a pendulum-type magnetometer (Manics DSM8) equipped with a helium continuous-flow cryostat under a magnetic field of approximately 1.5 T. Diamagnetic corrections were estimated from Pascal tables. The ESR spectra were recorded on a Bruker ES200 spectrometer at X-band frequency, with an Oxford liquid-helium cryostat for variable temperatures.

Crystallography

A prismatic crystal (0.20 × 0.10 × 0.10 mm) of complex **1** was selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($12 \leqslant \theta \leqslant 21$) and refined by least-squares methods. Intensities were collected with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.710\,69$ Å), using the ω–2θ scan technique. 5505 Reflections were measured in the range $1.77 \leqslant \theta \leqslant 29.94°$, 3095 of which were assumed as observed [$I \geqslant 2\sigma(I)$]. Three reflections were measured every 2 h as orientation and intensity control; no significant decay was observed. The crystallographic data and some features of the structure refinement are listed in Table 1. Lorentz-polarization but not absorption corrections were made. The structure was solved by Patterson synthesis using the SHELXS 86 computer program[16] and refined (on F^2) by full-matrix least squares using SHELXL 93[17] with 5455 reflections (very negative intensities were not employed). The function minimized was

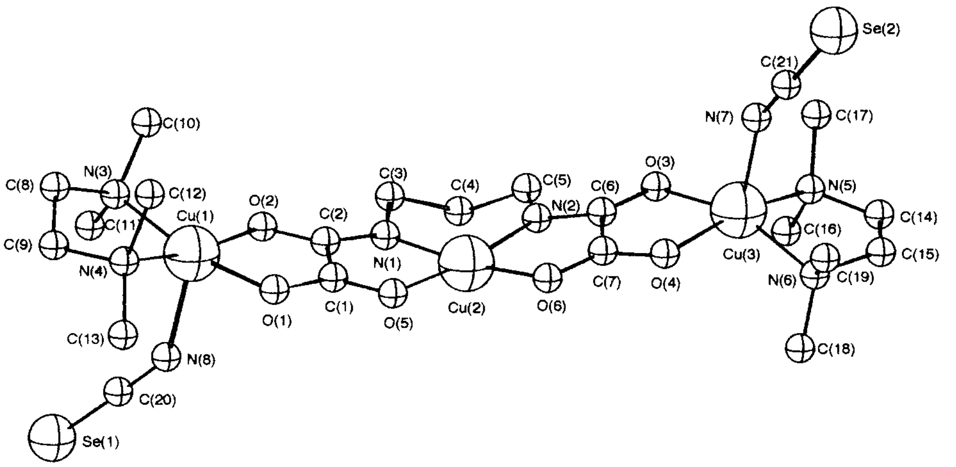

Fig. 1 Atom-labelling scheme for [{Cu(tmen)(SeCN)}$_2${μ-Cu(pba)}] **1**

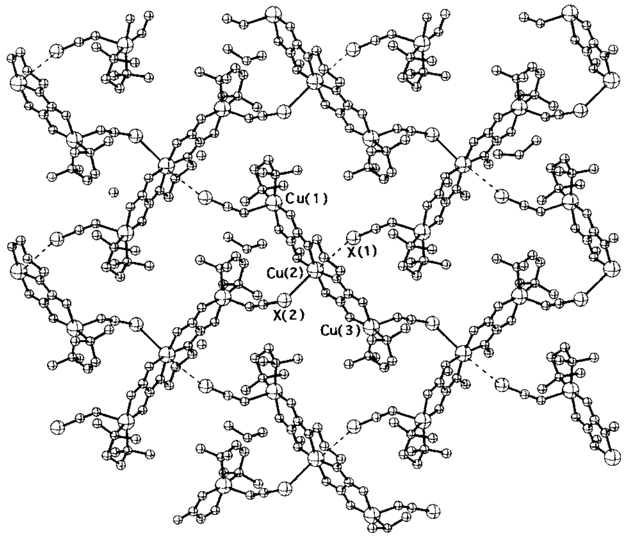

Fig. 2 View of the pseudo-two-dimensional entity for complex **1** and its thiocyanato analogue; X represents S or Se. The distances between X and Cu(2) are: Cu(2)···S(1) 3.014, Cu(2)···S(2) 3.617; Cu(2)···Se(1) 3.059, Cu(1)···Se(2) 3.465 Å

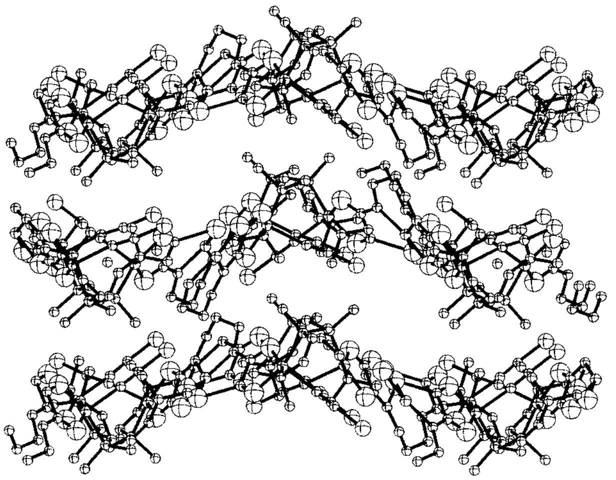

Fig. 3 View of the packing of the layers in complex **1**

Table 1 Crystallographic data for [{Cu(tmen)(SeCN)}$_2${μ-Cu(pba)}] **1**

Formula	$C_{21}H_{42}Cu_3N_8O_8Se_2$
M	883.17
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
T/°C	25
a/Å	12.444(6)
b/Å	14.309(3)
c/Å	19.303(5)
U/Å^3	3437(2)
Z	4
D_c/g cm^{-3}	1.707
μ(Mo-Kα)/cm^{-1}	4.009
$F(000)$	1772
No. parameters refined	381
R^a	0.052
$wR2^b$	0.147

$^a\ \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b\ \{\Sigma[(F_o)^2 - (F_c)^2]^2/\Sigma(F_o)^4\}^{\frac{1}{2}}$.

$\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = [\sigma^2(I) + (0.2335P)^2 + P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. Values of f, f' and f'' were taken from ref. 18. The extinction coefficient was 0.0003(4). The chirality of the structure was defined from the Flack[19] coefficient, which is equal to 0.01(3) for the results given. All H atoms were computed and refined with an overall isotropic thermal parameter, using a riding model. Maximum shift/e.s.d. = 0.33, mean shift/e.s.d. = 0.08. Maximum and minimum peaks in final difference synthesis 0.679 and −0.542 e Å^{-3} respectively. The high equivalent anisotropic thermal parameters for O(8), C(12), C(15), C(16) and C(18) show a possible disorder of these atoms.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/280.

Results and Discussion

Infrared spectrum

The IR spectrum of complex **1** shows the typical and strong band corresponding to the selenocyanate ligand at 2075 cm^{-1}, two other very strong bands centred at 1600 and 1620 cm^{-1} due to the co-ordinated oxamato group and between 1500 and 400 cm^{-1} there are many bands attributable to the co-ordinated amines.

Crystal structure

The trinuclear entity of compound **1** is shown in Fig. 1. The terminal copper(II) ions Cu(1) and Cu(3) have 4 + 1 co-ordination, their basal planes being formed by two nitrogen atoms from the tmen ligand, two oxygen atoms from the oxamate and one nitrogen from the selenocyanate. The central Cu(2) atom has quasi-square-planar co-ordination, with a weak tetrahedral distortion calculated as 0.9°. Selected bond

Table 2 Selected bond distances (Å) and angles (°) for compound **1**

Cu(1)–O(2)	1.988(7)	Cu(2)–O(5)	1.992(7)
Cu(1)–O(1)	2.000(7)	Cu(2)–O(6)	2.000(7)
Cu(1)–N(4)	2.016(9)	Cu(3)–O(4)	1.989(8)
Cu(1)–N(3)	2.051(8)	Cu(3)–O(3)	2.020(8)
Cu(1)–N(8)	2.23(2)	Cu(3)–N(6)	2.030(8)
Cu(2)–N(2)	1.952(8)	Cu(3)–N(5)	2.060(9)
Cu(2)–N(1)	1.957(7)	Cu(3)–N(7)	2.180(11)
O(2)–Cu(1)–O(1)	85.6(3)	N(1)–Cu(2)–O(5)	84.7(3)
O(1)–Cu(1)–N(4)	93.5(3)	N(2)–Cu(2)–O(6)	85.0(3)
O(2)–Cu(1)–N(3)	90.9(3)	N(1)–Cu(2)–O(6)	171.7(4)
O(1)–Cu(1)–N(3)	167.3(4)	O(4)–Cu(3)–O(3)	83.8(3)
N(4)–Cu(1)–N(3)	87.6(4)	N(5)–Cu(3)–N(7)	99.1(4)
N(3)–Cu(1)–N(8)	98.0(4)	O(4)–Cu(3)–N(7)	96.5(5)
O(2)–Cu(1)–N(8)	94.2(5)	O(3)–Cu(3)–N(6)	155.5(4)
O(1)–Cu(1)–N(8)	94.5(4)	O(4)–Cu(3)–N(5)	164.4(4)
N(4)–Cu(1)–N(8)	96.6(5)	O(3)–Cu(3)–N(5)	91.9(3)
O(2)–Cu(1)–N(4)	169.2(4)	O(4)–Cu(3)–N(6)	91.4(3)
N(2)–Cu(2)–N(1)	94.4(3)	O(3)–Cu(3)–N(7)	106.2(4)
N(2)–Cu(2)–O(5)	170.5(4)	N(6)–Cu(3)–N(5)	86.4(3)
O(5)–Cu(2)–O(6)	94.5(3)	N(6)–Cu(3)–N(7)	98.2(4)

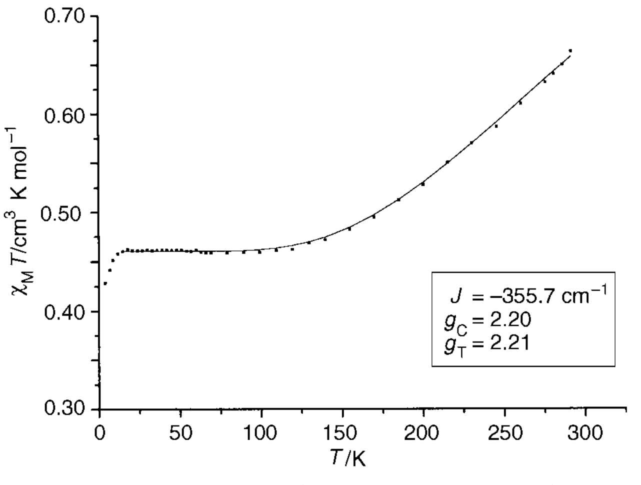

Fig. 4 Magnetic susceptibility of a polycrystalline sample of complex **1**. The solid line shows the best fit from the expression for the magnetic susceptibility of an isotropically coupled copper(II) trimer

distances and angles are given in Table 2. All are very similar to those reported for the perchlorate[2] and thiocyanato [1] analogues. The Cu···Cu separations within the trinuclear unit are Cu(1)···Cu(2) 5.21 and Cu(2)···Cu(3) 5.22 Å. The selenium atoms are weakly linked to a central Cu(2) of other trinuclear entities: Cu(2)···Se(1) 3.06 and Cu(2)···Se(2) 3.46 Å giving a one(two)-dimensional structure shown in Fig. 2. The angles in the bridge Cu(2)–SeCN–Cu(1,3) are as follows: Cu(3)–N–C 155.1 and Cu(2)–Se(2)–C 110.9° (in the moiety with short distance Cu···Se 3.06 Å) and Cu(1)–N–C 143.9 and Cu(2)–Se(1)–C 130.9° (in the moiety with long distance Cu···Se 3.46 Å). These pseudo-two-dimensional layers are linked in the crystal (Fig. 3) by van der Waals forces.

Magnetic properties

Susceptibility measurements of [{Cu(tmen)(SeCN)}$_2${μ-Cu(pba)}] are plotted in Fig. 4 as $\chi_m T$ *vs.* T. From room temperature down to 25 K there is a clear decrease in $\chi_m T$ values, followed by a plateau close to 0.45 cm^3 K mol^{-1}, a typical value for an isolated copper(II) trimer ($S = \frac{1}{2}$), assuming antiferromagnetic coupling between the copper(II) ions.[2] At low temperature $\chi_m T$ decreases, as with the similar thiocyanato analogue.[1] Taking into account the structure, also very similar, we can propose the same hypothesis: a small ferromagnetic coupling between trimers due to the selenocyanate bridging ligands.[1,3–11] Indeed, in all complexes with thiocyanate or selenocyanate as bridging ligands the bond angles M–N–C and M–S(Se)–C are relatively close to 180 and 90° respectively. In our case these angles are 155.1 and 111° respectively (considering that a bond forms when the distance Cu···Se is 3.0 Å, but not at 3.47 Å). Ginsberg *et al.*[7] and Duggan and Hendrickson[8] developed a valence bonding model by applying the Goodenough–Kanamori rules[20] or Anderson's expanded orbital theory[21] to demonstrate the ferromagnetism of these pseudohalide complexes. The closer to those values (180 and 90°) the stronger is the ferromagnetic coupling. In our case this coupling should be weak. With this hypothesis the total $\chi_m T$ value should tend to zero at 0 K, as is observed experimentally.

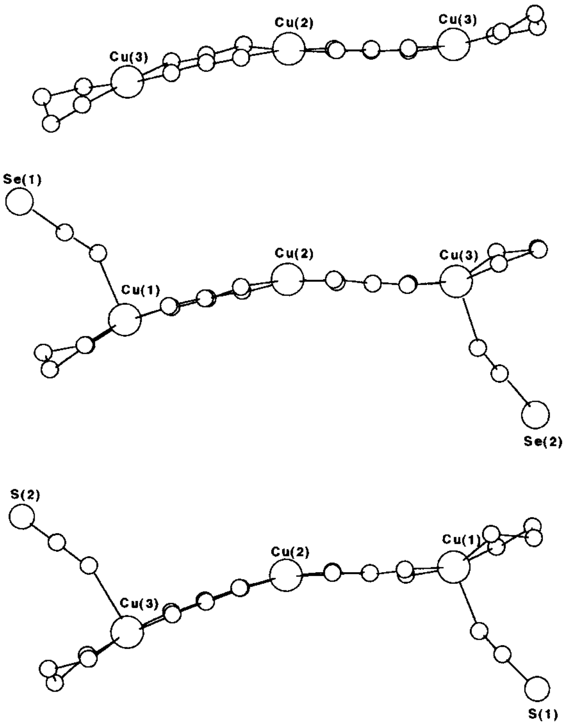

Fig. 5 Schematic representation (taken from crystal data) of the three complexes, perchlorate (top), selenocyanate (middle) and thiocyanate (bottom)

The experimental data (from room temperature to 20 K) were fitted using the theoretical expression deduced from the spin Hamiltonian (1) with $T1$ and $T2$ being the terminal copper(II) ions and C the central one. In this Hamiltonian the interaction between the terminal ions is assumed to be nil. The mathematical expression is given in ref. 2. Minimizing

$$H = -J[S_{T1}S_C + S_C S_{T2}] + \beta H[g_T(S_{T1} + S_{T2}) + g_C S_C] \quad (1)$$

$R = \Sigma[(\chi_m T)^{obs} - (\chi_m T)^{calc}]^2/\Sigma[(\chi_m T)^{obs}]^2$ leads to the values $J = -355.7$ cm^{-1}, $g_C = 2.20$ and $g_T = 2.21$. The g value obtained from the powder EPR spectra at room temperature is 2.13. The band is very broad and isotropic; at lower temperature the signal becomes sharp and anisotropic, with $g_\perp = 2.30$ and $g_\parallel = 2.15$ at 4 K. As previously pointed out[2] it is highly probable that the intermolecular exchange-averaging condition is always fulfilled for trinuclear copper(II) compounds. This shows that special care should be exercised when interpreting powder spectra of such complexes.

Comparison with perchlorate and thiocyanate analogues. Comparing J values for the three complexes (perchlorate, thiocyanate and selenocyanate), small (but significant) differences are found: $J = -380$, -332 and -356 cm^{-1}, respectively. There

Table 3 Main molecular parameters which affect the antiferromagnetic coupling for the three similar complexes (perchlorate, selenocyanate and thiocyanate)

					Deviation[c]/Å		
	J/cm^{-1}	Cu–Cu–Cu/°	Planes angle[a]/°	Torsion at Cu(2)[b]/°	Cu(2)	Cu(1)	Cu(3)
ClO_4^-	−380	169.5	164.7	6.29	0.034	−0.107	−0.004
$SeCN^-$	−356	165.6	163.3	0.9	−0.153	−0.204	0.351
SCN^-	−332	163.3	160.7	1.2	−0.153	0.363	0.128

[a] Formed by the two mean oxamato-like planes which contain the copper(II) ions. [b] Square planar ⟷ tetrahedral distortion. [c] Deviation of the copper(II) ion from the mean plane created by the four basal atoms (in square-planar or square-pyramidal co-ordination).

is, thus, a gradual decrease in the order ClO_4^- > $SeCN^-$ > SCN^-. The J variation from one complex to another is *ca.* 30 cm^{-1}. Fig. 5 shows a schematic representation (taken from crystal data) of the three complexes, and in Table 3 we have gathered the most significant differences between them. As previously reported[2] the most antiferromagnetic coupling occurs when the trinuclear entity is completely planar assuming that all copper(II) ions are in the centre of the square-planar co-ordination. This is an ideal case, not found even in the perchlorate. From Table 3 it is seen that the perchlorate has the smallest deviations from the co-ordination planes, but the torsion (square planar–tetrahedral) in Cu(2) is the greatest (6.29°); in contrast, this torsion for the thiocyanate and selenocyanate is less pronounced (only 1°) but the deviations from the mean planes for Cu(1), Cu(2) and Cu(3) are more marked and almost equal for both pseudohalides. Thus, the most important difference between the three complexes lies in the angles formed by the three copper(II) ions and/or in the angles formed by the two mean oxamato-like planes [which contain the copper(II) ions]. These angles create a deviation from planarity in the order SCN^- > $SeCN^-$ > ClO_4^-, which may be the main factor that diminishes the antiferromagnetic coupling because it reduces the overlap between magnetic orbitals. The experimental J values are consistent with this explanation.

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