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Spectroscopy and structures of two complete families, one mononuclear, the other binuclear, of 1 : 2 CuX : dptu stoichiometry (X = Cl, Br, I; 'dptu' = *N*,*N′*-diphenylthiourea)†

Graham A. Bowmaker,[*a] **Narongsak Chaichit,**[b] **John V. Hanna,**[c] **Chaveng Pakawatchai,**[d] **Brian W. Skelton**[e] **and Allan H. White**[e]

Received 8th May 2009, Accepted 14th July 2009
First published as an Advance Article on the web 13th August 2009
DOI: 10.1039/b909167j

Crystallization of the copper(I) halides (CuX; X = Cl, Br, I) with *N*,*N′*-diphenylthiourea ('dptu' = $(PhNH)_2CS$) in 1 : 2 ratio from acetonitrile solution in ambient conditions yields a mononuclear isomorphous series of complexes of the form $[XCu(dptu)_2]\cdot H_2O$, an unusually complete array, with the central copper atoms in *quasi*-trigonal planar environments, as shown by single crystal X-ray studies, in turn providing a platform for comparative spectroscopic studies. Under anhydrous conditions, anhydrous compounds may be obtained, a full series again being accessible, but now of the binuclear form $[(dptu)XCu(\mu\text{-}S\text{-}dptu)_2CuX(dptu)]$, the chloride being a bis(acetonitrile) solvate, the isomorphous bromide and iodide pair being unsolvated. A (solvated) sulfate salt is found to be of the form $[Cu(dptu)_2]_2(SO_4)$, providing a novel example of a copper(I) atom being (*quasi*-)linearly coordinated by the pair of unidentate (dptu) sulfur ligands, Cu–S 2.1770(5), 2.1811(5) Å, S–Cu–S 162.18(2)°. The $\nu(CuX)$ vibrational frequencies are assigned in the far-IR spectra of $[XCu(dptu)_2]\cdot H_2O$ (X = Cl, Br, I) at 274, 207, and 190 cm^{-1} respectively. The broadline static ^{65}Cu NMR spectra of $[Cl_2Cu_2(dptu)_4]\cdot 2CH_3CN$ and $[X_2Cu_2(dptu)_4]$ (X = Br, I) have been recorded at 9.4 and 7.05 T, and the spectra have been analysed to yield the ^{65}Cu nuclear quadrupole coupling and chemical shift parameters. The $^{63,65}Cu$ nuclear quadrupole resonance frequencies of $[XCu(dptu)_2]\cdot H_2O$ (X = Cl, Br, I) have also been measured, and the resulting ^{65}Cu quadrupole coupling constants are *ca.* 4× those of the dimeric $[X_2Cu_2(dptu)_4]$ compounds.

Introduction

In a recent report[1] we have summarized at some length the fascinating array of complexes formed between simple salts of copper(I), CuX, and (simple substituted) thiourea ligands, L (= (x)tu), these varying from simple mononuclear complexes, of form CuX : (x)tu (1 : *n*), (being $[XCuL_n]$ or $[CuL_n]X$ in form), to complex oligonuclear arrays, some of high putative symmetry. Among the former, despite the number and variety of systems studied, there is a dearth of any series with a constant familial relationship across arrays of the type $[XCuL_n]$, permitting comparison of the effect of variation in X on bonding parameters of the array. (There is an isomorphous (tetragonal) series for adducts of CuX (X = Cl, Br, I) with the parent tu, of 1 : 3 stoichiometry, but that array is ionic $[Cu(tu)_3]^+_{(\infty|\infty)}X^-$, so that the variation in halide ion impacts less emphatically on the form of the complex, which is a cationic polymer, devoid of halide, which is the counterion.[2]) With *N*,*N′*-diphenylthiourea, ('dptu' = $(PhNH)_2CS$), we have now obtained, with CuX (X = Cl, Br, I), two series of complexes of 1 : 2 CuX : dptu stoichiometry, one an isomorphous mononuclear series, of the form $[XCuL_2](\cdot H_2O)$, defined by single crystal X-ray structure determinations, which provide platforms for analytical spectroscopic studies of these arrays; the structure of the $[Cu(dptu)_2]^+$ cation, defined in a solvated sulfate salt, provides a useful *quasi*-linear two-coordinate 'baseline' comparator. On preparing bulk samples for spectroscopy, it was found that initial results were inconsistent with expectations from the structural results, further work showing that, working more rapidly with more concentrated solutions, anhydrous compounds were obtained, also of similar form, across all X = Cl, Br, I (albeit not all isomorphous), but, remarkably, all binuclear, of the form $[(dptu)XCu(\mu\text{-}S\text{-}dptu)_2CuX(dptu)]$, providing examples of a full series for that form also. We report this work hereunder.

Experimental

Synthesis

Dichlorotetrakis(diphenylthiourea)dicopper(I) bis(acetonitrile) solvate, $[Cl_2Cu_2(dptu)_4]\cdot 2CH_3CN$. A mixture of copper(I)

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[a] *Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand. E-mail: ga.bowmaker@auckland.ac.nz; Fax: +64 9 373 7422; Tel: +64 9 373 7599 ext. 88340*
[b] *Physics Department, Thammasat University Rangsit, Pathumthani 12121, Thailand*
[c] *Department of Physics, University of Warwick, Gibbet Hill Rd., Coventry, UK CV4 7AL*
[d] *Department of Chemistry, Prince of Songkla University, Hat-Yai 90112, Thailand*
[e] *Chemistry M313, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, Crawley 6009, Western Australia, Australia*

† CCDC reference numbers 660459–660462 and 671528–671530. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b909167j

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chloride (0.50 g, 5 mmol) and diphenylthiourea (2.28 g, 10 mmol) in acetonitrile (16 ml) was heated with stirring until all of the solids dissolved, yielding a yellow solution which deposited yellow crystals of the product upon cooling. Yield 2.64 g (89%). Anal. calcd for $C_{56}H_{54}Cl_2Cu_2N_{10}S_4$: C, 56.36; H, 4.56; N, 11.74%. Found: C, 56.2; H, 4.8; N, 11.5%.

Dibromotetrakis(diphenylthiourea)dicopper(I), $[Br_2Cu_2(dptu)_4]$. A mixture of copper(I) bromide (0.72 g, 5 mmol) and diphenylthiourea (2.28 g, 10 mmol) in acetonitrile (30 ml) was heated with stirring to boiling, yielding a yellow solution which deposited pale yellow crystals upon cooling. Yield 2.79 g (93%). Calcd for $C_{52}H_{48}Br_2Cu_2N_8S_4$: C, 52.04; H, 4.03; N, 9.34%. Found: C, 52.3; H, 4.3; N, 9.5%.

Diiodotetrakis(diphenylthiourea)dicopper(I), $[I_2Cu_2(dptu)_4]$. A mixture of copper(I) iodide (0.95 g, 5 mmol) and diphenylthiourea (2.28 g, 10 mmol) in acetonitrile (40 ml) was heated with stirring to boiling. The solution turned yellow and a microcrystalline pale yellow solid formed. Further pale yellow solid formed upon cooling. Yield 3.06 g (95%). Calcd for $C_{52}H_{48}Cu_2I_2N_8S_4$: C, 48.26; H, 3.74; N, 8.66%. Found: C, 48.5; H, 4.0; N, 8.8%.

Halogenobis(diphenylthiourea) copper(I) monohydrate, $[XCu(dptu)_2]\cdot H_2O$ (X = Cl, Br, I). Originally these were obtained straightforwardly as nicely crystalline solids by dissolving *ca.* 10 mmol (*ca.* 2.3 g) of diphenylthiourea together with 5 mmol of the copper(I) halide in acetonitrile (*ca.* 100 ml), with warming and stirring; the yellow solutions were filtered and allowed to stand in ambient conditions, depositing, after some time, colourless crystals of $[XCuL_2]\cdot H_2O$ suitable for the X-ray work. (Mp X = Cl, Br, I: 169–171, 187–190, 193–195 °C, respectively). Bulk samples for spectroscopic studies were subsequently made by the deliberate addition of water to hot solutions of $[X_2Cu_2(dptu)_4]$ in acetonitrile, the water content being 10–20% by volume. The colourless crystalline products separated upon cooling, with yields >90%. Anal. X = Cl, calcd for $C_{26}H_{26}CuClN_4OS_2$: C, 54.44; H, 4.57; N, 9.77%. Found: C, 54.4; H, 4.7; N, 9.9%; X = Br, calcd for $C_{26}H_{26}BrCuN_4OS_2$: C, 50.52; H, 4.24; N, 9.06%. Found: C, 50.8; H, 4.5; N, 9.3%; X = I, calcd for $C_{26}H_{26}CuIN_4OS_2$: C, 46.95; H, 3.94; N, 8.42%. Found: C, 47.1; H, 4.2; N, 8.6%.

Attempts to obtain useful crystals of the 1 : 2 sulfate salt (as an example of a species likely to yield a linearly coordinated $[Cu(dptu)_2]^+$ array in the presence of a non- or poorly-coordinating counterion) by commencing with an appropriate stoichiometry of copper(II) sulfate, also in acetonitrile, were generally unsuccessful; on one occasion a few small crystals were obtained after prolonged standing in ambience, shown by a diffraction study to essentially be such a material, containing cocrystallized/‘solvating’ PhNCS, presumably arising from degradation of the ligand upon standing in ambience. Attempts to prepare 1 : 2 or 1 : 3 sulfate or nitrate salts by reaction of cuprous oxide and diphenylthiourea in bulk in the appropriate molar ratios with sulfuric or nitric acid in acetonitrile resulted in yellow solutions from which only yellow oils separated upon evaporation of the solvent.

Structure determinations

Full spheres of CCD area-detector diffractometer data were measured (ω-scans; monochromatic Mo-Kα radiation, λ = 0.71073 Å), $N_{t(otal)}$ reflections merging to N unique (R_{int} cited) after ‘empirical’/multiscan absorption correction (proprietary software) (N_o with $F > 4\sigma(F)$ considered ‘observed’), which were used in the full matrix least squares refinements on F^2, refining anisotropic displacement parameter forms for the non-hydrogen atoms, hydrogen atoms being included following a riding model (reflection weights: $(\sigma^2(F_o^{\,2}) + (aP)^2\ (+\ bP))^{-1}$, $(P = (F_o^{\,2} + 2F_c^{\,2})/3)$). Neutral atom complex scattering factors were employed within the SHELXL 97 program.[3] Pertinent results are given below and in the Tables and Figures, the latter showing 20% (298 K), 50% (153, 100 K) probability amplitude displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å (where shown). See Table 1 for crystal structure and refinement data.

Infrared spectroscopy

Infrared spectra were recorded at 4 cm^{-1} resolution as Nujol mulls between KBr plates on a Perkin Elmer Spectrum 1000 Fourier-transform infrared spectrometer. Far-infrared spectra were recorded using a Nicolet 8700 FTIR spectrometer on samples suspended in Polythene disks.

^{65}Cu broadline NMR and $^{63/65}$Cu NQR spectroscopy

Static broadline ^{65}Cu NMR data were acquired at ambient temperatures on 7.1 T and 9.4 T systems using Varian Infinity Plus-300 and Bruker DSX-400 spectrometers operating at ^{65}Cu Larmor frequencies of 85.20 MHz and 113.67 MHz, respectively. These measurements were performed using Bruker 5/7.5 mm static horizontal solenoid design probes. All static ^{65}Cu data were acquired with the solid echo θ–τ–θ–τ–(acquire) experiment with an extended phase cycle to capture undistorted echoes with minimal influence from residual echo tails.[4,5] ‘Non-selective’ (solution) $\pi/2$ pulse times of 2 µs were calibrated on a solid Cu(I)Cl sample from which a ‘selective’ (solid) θ pulse of 0.6 µs was employed in all solid echo measurements. The τ delay was 20 µs and the relaxation delay between transients was 0.5 s. Measurements at 9.4 T required one on-resonance experiment to uniformly excite the central ($-1/2\leftrightarrow+1/2$) transition resonances. However the broader 7.1 T resonances required recourse to the VOCS (Variable Offset Cumulative Spectroscopy) technique to add frequency-offset subspectra, thus ensuring the acquisition of undistorted lineshapes.[6–8] This method entails the stepping of the solid echo experiment through a suitable number of carrier frequencies (typically offset by 100 kHz) to uniformly excite the full width of each central transition resonance. For these 7.1 T data, co-addition of five subspectra (after shifting to a common spectral reference) provided an undistorted representation of each broad lineshape. All ^{65}Cu isotropic chemical shifts δ_{iso} are referenced directly to Cu(I)Cl, which was assigned to δ 0.0 ppm. The ^{65}Cu signal in Cu(I)Cl was measured at δ –337.0 ppm relative to the primary standard saturated $[Cu(CH_3CN)_4]ClO_4$ in dry CH_3CN at 20 °C. All ^{65}Cu static broadline spectra were simulated with the Bruker TOPSPIN solids package and the QUASAR solid state NMR data simulation program[9] to deconvolute the nuclear quadrupole and chemical shift anisotropy components contributing to these lineshapes. This treatment facilitated an accurate measurement of the isotropic chemical shift (δ_{iso}), quadrupole coupling constant (C_Q), nuclear quadrupole asymmetry parameter (η_Q), chemical

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Table 1 Crystal/refinement data

	Mononuclear arrays $C_{26}H_{26}XCuN_4OS_2$, $[XCu(dptu)_2]\cdot H_2O$				Binuclear arrays $C_{52}H_{48}X_2Cu_2N_8S_4$, $[(dptu)XCu(\mu\text{-}S\text{-}dptu)_2CuX(dptu)]$		
	Cl	Br	I	SO_4[a]	Cl[b]	Br	I
M_r/Da	573.7	618.1	665.1	611.0	1193.3	1200.2	1294.1
Crystal system	Triclinic	Triclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	*Pnma* (#62)	$P2_1/c$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a/Å	9.4076(5)	9.4378(5)	9.5132(3)	17.367(1)	12.3405(1)	11.8704(2)	11.9993(2)
b/Å	12.0075(6)	12.1456(6)	12.4449(3)	24.495(2)	12.1787(1)	12.2178(1)	12.1609(3)
c/Å	12.6204(4)	12.6684(4)	12.7948(2)	13.292(1)	18.4154(2)	18.0909(3)	18.4265(4)
α/°	89.217(3)	90.047(3)	91.807(2)				
β/°	73.998(3)	73.966(3)	73.165(2)		92.551(1)	106.214(1)	106.447(2)
γ/°	69.361(4)	69.386(4)	69.216(2)				
V/Å^3	1277	1299	1340	5655	2765	2519	2579
D_c/g cm^{-3}	1.492	1.581	1.648	1.435	1.433	1.582	1.667
Z	2	2	2	8	2	2	2
μ_{Mo}/mm^{-1}	1.15	2.6	2.1	1.011	1.065	2.6	2.23
Specimen/mm	0.26,0.18,0.03	0.34,0.33,0.055	0.26,0.20,0.03	0.25,0.21,0.18	0.17,0.16,0.12	0.18,0.11,0.08	0.15,0.13,0.04
$T_{min/max}$	0.99	0.62	0.64	0.84	0.91	0.87	0.89
$2\theta_{max}$/°	67.5	67.5	75	57	70	70	75
N_t	24 509	27 220	47 834	65 458	50 097	89 483	56 745
N (R_{int})	10 140 (0.049)	12 945 (0.039)	13 635 (0.051)	7472 (0.029)	11 555 (0.045)	10 683 (0.061)	13 255 (0.045)
N_o	5615	8308	8846	5929	7715	7071	7367
R_1	0.039	0.034	0.032	0.035	0.030	0.028	0.048
wR_2	0.090	0.095	0.090	0.099	0.070	0.060	0.123
a(, b)	0.039	0.045	0.048	0.054, 2.39	0.035	0.028	0.052, 1.22
S	0.84	1.00	0.95	1.04	0.94	0.94	1.056
T/K	100	100	100	153	100	100	100

[a] This complex was modeled as $[Cu(dptu)_2](SO_4)_{0.5}\cdot(H_2O)_{0.5}\cdot(PhNCS)_{0.25} \equiv C_{27.75}H_{26.25}CuN_{4.25}O_{2.5}S_{2.75}$. Phenyl ring 41 was modeled as disordered over two sets of sites of equal occupancy, concerted with a pair of residues modeled as water molecule oxygen atom fragments. Site occupancy of the PhNCS residue was set at 0.5 after trial refinement; it, the water molecule components and SO_2 of the anion lie in the crystallographic mirror plane. [b] The complex is an acetonitrile di-solvate, $C_{56}H_{54}Cl_2Cu_2N_{10}S_4$.

shift anisotropy ($\Delta\delta$)/chemical shift span (Ω) and asymmetry (η_δ)/skew (κ), and the Euler angles α,β,γ relating the nuclear quadrupole and chemical shift tensor frames.

^{63}Cu and ^{65}Cu NQR frequencies ($\nu_{Q,^{63}Cu}$ and $\nu_{Q,^{65}Cu}$) were obtained at ambient temperature by solid echo pulse methods using a Chemagnetics CMX-200 console which delivered high-power rf pulses into a probe arrangement that was shielded from extraneous magnetic and rf interference by a mumetal container. Similar solid echo experiments with extended phase cycles to those outlined above were implemented for these measurements, utilizing power levels of ~600 $V_{p\text{-}p}$ (*i.e.* ~212 V_{rms} or 940 W) and recycle delays 0.5 s. The values of $\nu_Q(^{63}Cu)$ obtained from the ^{63}Cu nuclei were verified by measurement of the corresponding $\nu_Q(^{65}Cu)$ from the ^{65}Cu nuclei which are related by the ratio of the nuclear quadrupole moments (Q):

$$\nu_Q(^{63}Cu)/\nu_Q(^{65}Cu) = Q(^{63}Cu)/Q(^{65}Cu) = 1.0806 \qquad (1)$$

This ensured that all reported NQR frequencies were correctly attributed to Cu nuclei, thus eliminating the possibility of associating a measured frequency with an energy level transition from other quadrupolar nuclei in each sample.

Results and discussion

X-Ray structures

$[XCu(dptu)_2]\cdot H_2O$ (X = Cl, Br, I) crystallize with one formula unit, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. Within each ligand, one of the NH groups (# n2) hydrogen bonds intramolecularly to the halide atom, while the n1 NH groups hydrogen bond to the water molecule oxygen atom, catenating thus (Fig. 1). Although there is some variation in the disparity in the X–Cu–S pair of angles along the series, S–Cu–S is essentially constant, Cu–S exhibiting a slight increase on passing from chloride to iodide (Table 2).

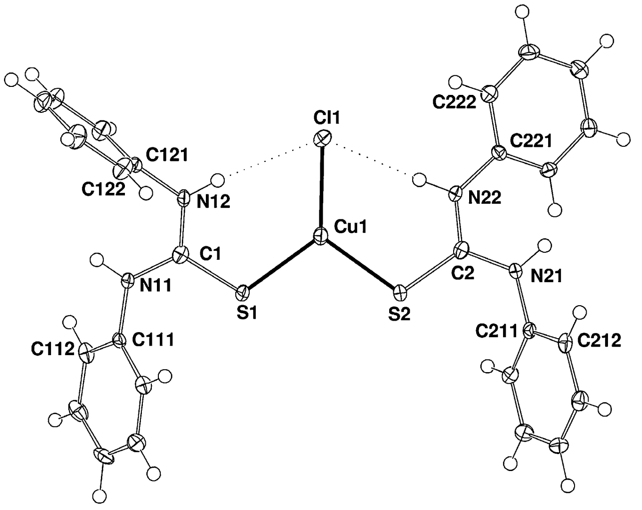

Fig. 1 Projection of a single molecule of $[ClCu(dptu)_2]$ normal to the coordination plane.

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Table 2 Selected geometries [XCu(dptu)$_2$] (X = Cl, Br, I) The three values in each entry are for X = Cl, Br, I, respectively

Atoms	Parameter
Distances/Å	
Cu–X	2.2269(6), 2.3575(2), 2.5227(3)
Cu–S(1)	2.2046(5), 2.2114(2), 2.2276(5)
Cu–S(2)	2.2265(6), 2.2261(2), 2.2380(5)
Angles/°	
X–Cu–S(1)	127.28(2), 125.575(7), 125.31(2)
X–Cu–S(2)	124.68(2), 125.986(6), 128.05(2)
S(1)–Cu–S(2)	108.04(2), 108.433(7), 106.62(2)
Cu–S(1)–C(1)	111.18(6), 111.91(2), 112.43(7)
Cu–S(2)–C(2)	108.99(8), 119.94(2), 110.96(7)
Out-of-plane (SCN$_2$) copper atom deviations (δCu/Å)	
Plane 1	0.142(3), 0.173(2), 0.248(3)
Plane 2	0.497(3), 0.506(2), 0.511(3)
Core (XCuS$_2$)/ligand (SCN$_2$) interplanar dihedral angles/°	
Ligand 1	16.95(5), 18.04(4), 20.89(6)
Ligand 2	16.22(6), 16.10(4), 15.86(7)
Intraligand SCN$_2$/C$_6$(ar) interplanar dihedral angles/°	
Ligand 1/Ph(1)	63.18(7), 62.39(4), 63.16(8)
Ligand 1/Ph(2)	88.51(9), 88.88(4), 89.72(9)
Ligand 2/Ph(1)	53.81(7), 53.04(4), 51.51(7)
Ligand 2/Ph(2)	40.13(8), 39.01(4), 40.83(9)
Hydrogen bonds: intramolecular/Å	
X···N(12)	3.526(2), 3.5673(5), 3.684(2)
X···H(12)	2.7, 2.7, 2.8
X···N(22)	3.257(2), 3.510(6), 3.656(2)
X···H(22)	2.4, 2.6, 2.8
Hydrogen bonds: other/Å	
O···N(11^{i})	2.920(2), 2.9269(7), 2.930(2)
O···H(11^{i})	2.1, 2.1, 2.1
O···N(21^{ii})	3.005(2), 3.0005(6), 3.010(2)
O···H(21^{ii})	2.3, 2.3, 2.3

Transformations of the asymmetric unit: ^{i} $1-x, 1-y, \bar{z}$; ^{ii} $\bar{x}, 1-y, 1-z$.

Curiously, although a number of other adducts of mononuclear 1 : 2 CuX : L composition have been structurally defined (Table 3), all are of the form L = (substituted) etu, with, also, a pair of ptu (SC(NHCH$_2$)$_2$CH$_2$), with an angular constraint at the SC carbon atom imposed by the five- (or six-) membered rings. All of the pertinent NQR studies are drawn from those examples also (the NQR studies being conducted in tandem with the structure determinations).[17–19] The coordination environment parameters of these systems are also presented in Table 3. The scatter in comparable parameters is large, the comparison unassisted by data for any common ligand L across X = Cl, Br, I, except in the present array. For the L = xetu, X = Cl adducts, Cu–Cl distances range between 2.238(2)–2.279(2) with the mmetu example at the lower limit, in turn just higher than the present value of 2.2269(6) Å, which is the shortest of all. By contrast the value for the ptu complex is the longest (2.317(3) Å). The values of Cu–S are more closely ranged, albeit between 2.205(2)–2.230(2) Å with the extremal values being pertinent to the one compound (L = ipetu). The S–Cu–S angles range between 118.23(6)–121.9(1)°, but with that for the mmetu example outstandingly large at 134.2(1)°, presumably in consequence of steric hindrance between ligands, the ptu example also slightly enlarged at 123.4(1)°. The value for the present dptu complex is by far the smallest at 108.63(6)°. These considerations have parallels for the X = Br, I arrays, where the body of data is more limited.

In keeping with previous studies obtaining CuX : L (1 : n) complexes in ionic form with uncoordinated counterion X which were successful using X = SO$_4$, we attempted to obtain such a 1 : 2 adduct with X = sulfate. Success here was not as clean as could be desired, a successful crystallization on a limited scale producing a few crystals of such an adduct but cocrystallized with a component readily identified as the ligand degradation product phenyl isothiocyanate, additional difference map residues being assigned as water molecule oxygen atom fragments, thus [Cu(dptu)$_2$](SO$_4$)$_{0.5}$(H$_2$O)$_{0.5}$(PhNCS)$_{0.25}$. This comprises the asymmetric unit of the structure: a single [Cu(dptu)$_2$]$^+$ cation devoid of crystallographic symmetry, a sulfate ion with an SO$_2$ component lying in the mirror plane of space group *Pnma* (the other pair of oxygen atoms symmetry related to either side), and phenylisothiocyanate and water molecule oxygen atom fragments also lying in the mirror plane (Fig. 2(a)).

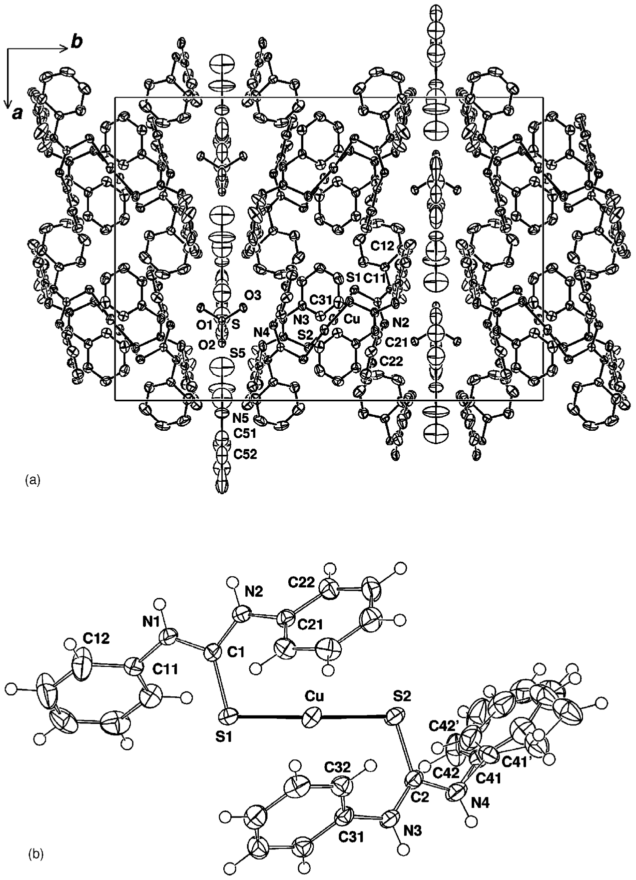

Fig. 2 (a) Unit cell contents of (solvated) [Cu(dptu)$_2$](SO$_4$)$_{0.5}$, projected down *c*. (b) Projection of the [Cu(dptu)$_2$]$^+$ cation.

Viewed appropriately (Fig. 2(b)), the cation has *quasi*-2 symmetry. Cu–S(1,2) are 2.1811(5), 2.1770(5) Å, *ca.* 0.05 Å less than the values observed in the [XCuL$_2$] neutral molecular adducts discussed above. S–Cu–S is 162.18(2)°, with Cu–S–C 104.76(6), 106.48(6)°. Although there are approaches to the copper atom from the shrouding phenyl rings 2 and 3 which might account for the above departure from S–Cu–S linearity (Cu···C(21, 26, 31, 32)

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Table 3 Structurally defined $[XCuL_2]$ systems: comparative copper(I) atom environments (Å, °)

Compound[a]	Cu–X	Cu–S	S–Cu–S	X–Cu–X
(a) X = Cl				
$[ClCu(metu)_2]$[10]	2.279(2)	2.217(1) (×2)	119.34(6)	120.33(3) (×2)
$[ClCu(eetu)_2]$[11]	2.238(2)	2.218(2), 2.214(2)	118.5(1)	121.4(1), 120.1(1)
$[ClCu(petu)_2]$[12]	2.257(2)	2.209(2), 2.223(3)	119.1(1)	120.6(1), 120.4(1)
(2 mol)	2.2693)	2.193(3), 2.223(2)	121.9(1)	120.7(1), 117.3(1)
$[ClCu(ipetu)_2]$[13]	2.246(2)	2.205(2), 2.230(2)	118.23(6)	122.85(6), 118.92(5)
$[ClCu(mmetu)_2]$[14]	2.233(3)	2.229(3) (×2)	134.2(1)	112.9(1) (×2)
$[ClCu(dptu)_2]$[b]	2.2269(6)	2.2046(5), 2.2265(6)	108.04(2)	127.28(2), 124.68(2)
$[ClCu(ptu)_2]$[15]	2.317(3)	2.206(2) (×2)	123.4(1)	118.3(1), 110.0(2)
(b) X = Br				
$[BrCu(eetu)_2]$[13]	2.366(2)	2.206(3), 2.210(2)	116.2(1)	120.69(8), 123.13(8)
$[BrCu(ipetu)_2]$[13]	2.372(1)	2.220(2), 2.220(2)	111.98(7)	123.34(6), 124.67(6)
$[BrCu(dptu)_2]$[b]	2.3575(2)	2.2114(2), 2.2261(2)	108.433(7)	125.575(7), 125.986(6)
$[BrCu(ptu)_2]$[16]	2.405(2)	2.215(4) (×2)	120.8(2)	119.6(1) (×2)
(c) X = I				
$[ICu(petu)_2]$[13,17]	2.531(2)	2.227(4), 2.240(4)	111.4(1)	122.5(1), 126.0(1)
$[ICu(dptu)_2]$[b]	2.5227(3)	2.2276(5), 2.2380(5)	106.62(2)	125.31(2), 128.05(2)

[a] Ligand abbreviations: xetu = $SCNR(CH_2)_2NH$, R = Me (x = m), Et (e), ${}^nPr$ (p), Pr (ip); mmetu = $SC(NMe(CH_2))_2$; ptu = $SC(NHCH_2)_2CH_2$. [b] This work.

2.798, 2.806, 2.867, 2.884(2) Å), the explanation may be more conveniently found to originate further afield in interactions of the NH hydrogen atoms pairwise with nearby sulfate groups, thus: $NH(1)\cdots O(2^i)$ 2.846(2), 1.98 (est.), $NH(2)\cdots O(3^i)$ 2.823(2), 1.95 (est.); $NH(3)\cdots O(3)$ 2.878(2), 2.04 (est.), $NH(4)\cdots O(1)$, 2.795(2), 1.99 Å (est.) (i ≡ $1\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$). S–O(1–3) are 1.480(2), 1.479(2), 1.475(1) (×2) Å, with O(1)–S–O(2, 3) 109.5(1), 108.8(1) (×2), O(2)–S–O(3) 109.14(7) (×2), O(3)–S–O(3) 111.5(1)°.

Examples of copper(I) linearly coordinated by a pair of unidentate thio ligands are surprisingly sparse, the present seemingly the first example of its type. Comparison may be made with the $[Cu(S{\cdot}CO{\cdot}Ph)_2]^-$ species,[20] wherein Cu–S are 2.151(3) Å, S–Cu–S 176.6(2)°, $[Cu(SAd)_2]^-$ (Ad ≡ adamantanyl) Cu–S 2.147(1) Å, S–Cu–S 180° [21] and, in a bis(*S*-dithiocarbamyl) environment, Cu–X 2.163(9) Å, S–Cu–S 180°,[22] all essentially harmonious with the present.

Working more rapidly, with more concentrated solutions to obviate the uptake of ambient moisture, procedures involving all of X = Cl, Br, I readily yield the adducts of 1 : 2 stoichiometry, this time in a new anhydrous form found to be binuclear $[(dptu)XCu(\mu\text{-}S\text{-}dptu)_2CuX(dptu)]$, a novel structural type (Fig. 3) previously only structurally defined in the 1 : 2 CuBr : etu adduct.[1] In all three complexes, the dimer is located about a crystallographic centre of symmetry, one half comprising the asymmetric unit of the structure; the bromide and iodide are isomorphous, but the chloride, although crystallizing in a similar cell, is solvated with well-defined acetonitrile, the molecular conformation being very similar to that of the other two. Yet again, as in the previous complexes and the parent ligand,[23] it appears that hydrogen bonding is an important contributor to the stability of the form: as in the etu/Br adduct, the halide ion is involved in intramolecular hydrogen bonds to each of the two ligands (Table 4). Perhaps in consequence of these and other lattice interactions, as in the etu/Br adduct, there are considerable distortions from mmm symmetry among the 'heavy atom' (X/Cu/S) core array; in the etu/Br adduct $Cu–S_b,S_b'$ are essentially equivalent, but 'equivalent' angles are perhaps more disparate than in the dptu/X counterparts, where the $Cu–S_b,S_b'$ distances differ appreciably. $Cu\text{-}X,S_t$ are appreciably longer (by *ca.* 0.06 Å) than in the $[XCu(dptu)_2]$ arrays, as befits the increase in coordination number from three to four.

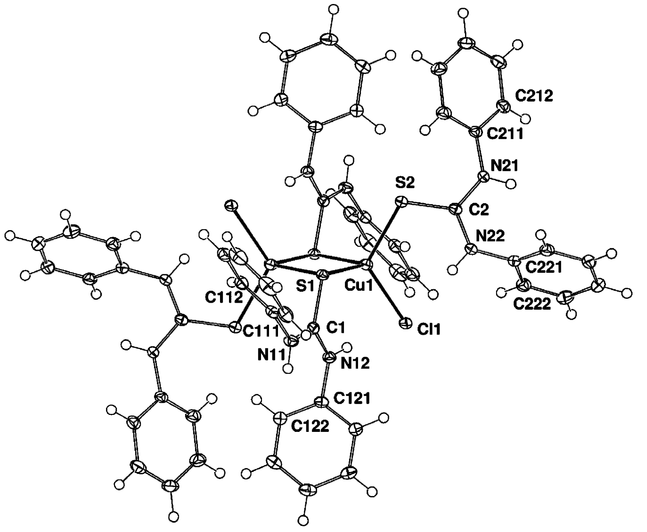

Fig. 3 Projection of binuclear $[(dptu)ClCu(\mu\text{-}S\text{-}dptu)_2CuCl(dptu)]$ oblique to the CuS_2Cu core plane.

IR spectroscopy

The far-IR spectra of the dptu ligand and of the complexes $[XCu(dptu)_2]{\cdot}H_2O$ (X = Cl, Br, I) are shown in Fig. 4. Diphenylthiourea shows several bands due to internal vibrational modes, but the region from 150 to 400 cm^{-1} is reasonably clear of strong ligand bands, providing an opportunity to detect the single *ν*(CuX) bands expected for the simple trigonal monomer structures in these complexes. According to previously established correlations between the Cu–X bond length and the *ν*(CuX) vibrational frequencies,[24] the frequencies corresponding to the Cu–X bond

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Table 4 Selected geometries, [(dptu)XCu(μ-*S*-dptu)$_2$CuX(dptu)$_2$] All species in this table are (crystallographically) centro-symmetric; inversion-generated atoms are denoted by a prime, b and t subscripts denoting bridging and terminal sulfur atoms

X	Cl	Br	I	Br[a]
Distances/Å				
Cu–X	2.3130(3)	2.4347(2)	2.6060(3)	2.4987(3)
Cu–S$_t$	2.2823(3)	2.2814(4)	2.2946(7)	2.2841(6)
Cu–S$_b$	2.3044(3)	2.3232(4)	2.3343(7)	2.3819(5)
Cu–S$_b$′	2.4698(3)	2.4840(4)	2.4928(7)	2.3851(5)
Cu···Cu′	2.9823(3)	3.0999(3)	3.0949(5)	2.7238(5)
S$_b$···S$_b$′	3.7319(4)	3.6777(5)	3.7078(9)	3.9122(7)
Angles/°				
Cu–S$_b$–Cu′	77.23(1)	80.23(1)	79.68(2)	69.69(2)
S$_b$–Cu–S$_b$′	102.77(1)	99.77(1)	100.32(2)	110.31(2)
S$_b$–Cu–S$_t$	106.60(1)	99.23(1)	99.98(2)	106.16(2)
S$_b$–Cu–X	115.90(1)	121.20(1)	120.89(2)	111.72(2)
S$_b$′–Cu–S$_t$	108.54(1)	106.14(1)	105.74(3)	112.75(2)
S$_b$′–Cu–X	103.60(1)	104.62(1)	103.82(2)	94.02(2)
S$_t$–Cu–X	118.10(1)	122.91(1)	123.12(2)	121.39(2)
Intramolecular hydrogen bonds/Å				
N(12)···X	3.256(1)	3.472(1)	3.590(2)	3.382(2)
H(12)···X	2.3_9	2.6_4	2.7_8	2.7_0
N(22)···X	3.198(1)	3.479(1)	3.607(2)	3.376(2)
H(22)···X	2.3_8	2.6_6	2.7_8	2.5_8

[a] Counterpart values for the etu/Br analogue (ref. 1).

lengths in Table 2 are 273, 208 and 181 cm^{-1} for X = Cl, Br, I respectively. Thus the bands at 274, 207, and 190 cm^{-1} (Fig. 4(b–d)) can be assigned to the *ν*(CuX) modes in these complexes. The *ν*(CuS) modes in copper(I) ethylenethiourea complexes have been assigned in the range 180–230 cm^{-1},[25] and corresponding vibrations involving the heavier dptu ligand are expected to occur in a lower frequency range. Bands observed in the range 115–160 cm^{-1} are in the right range to be thus assigned, but, because these occur in the same range as vibrational modes of the ligand (Fig. 4(a)), no definite assignments can be made.

The far-IR spectra of [Cl$_2$Cu$_2$(dptu)$_4$]·2CH$_3$CN and of [X$_2$Cu$_2$(dptu)$_4$] (X = Br, I) are shown in Fig. 5. From the Cu–X bond lengths in Table 4, *ν*(CuX) bands are expected at 227, 176 and 151 cm^{-1} for X = Cl, Br, I respectively. In the case of X = Cl, there is a definite band at 225 cm^{-1} (Fig. 5(a)) that can be assigned as *ν*(CuCl). For X = Br, I there are very weak bands at 175 and 146 cm^{-1}, respectively (Fig. 5(b, c), but these are not clear enough to allow unambiguous assignment.

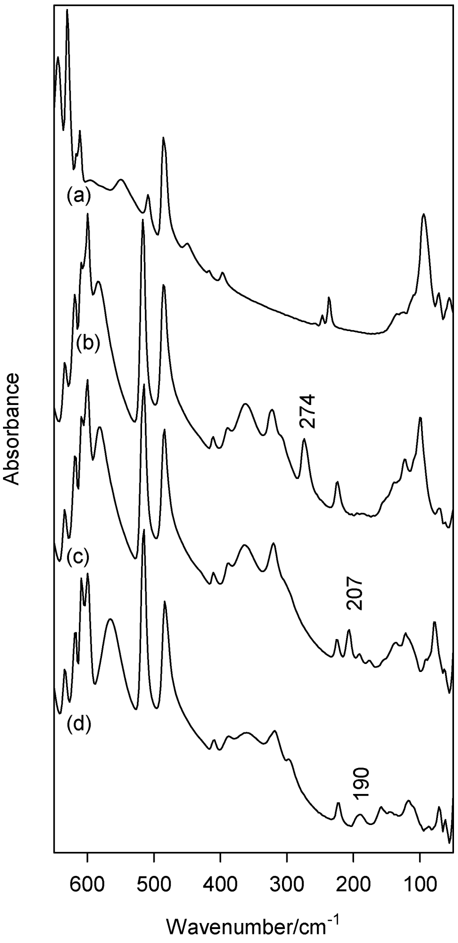

Fig. 4 Far-IR spectra of (a) the dptu ligand, and (b–d) [XCu(dptu)$_2$]·H$_2$O (X = Cl, Br, I). Bands assigned as *ν*(CuX) are labelled with their wavenumbers.

Broadline ^{65}Cu NMR spectroscopy

Despite the high natural abundance and the relatively high magnetic moments of the two naturally occurring isotopes of copper, ^{63}Cu (69.1%, $I = 3/2$) and ^{65}Cu (30.9%, $I = 3/2$), copper NMR spectra are usually difficult to record and interpret because of the large nuclear quadrupole coupling that is present in most copper compounds.[26a] Because of its lower nuclear quadrupole moment, ^{65}Cu is the preferred copper nuclide for NMR studies, despite its lower natural abundance. In compounds where the Cu atom lies on a site of nearly exact tetrahedral symmetry, the Cu quadrupole coupling constant C_Q is very small, and the ^{65}Cu NMR spectrum of a static powder sample shows a relatively sharp central (−1/2↔1/2) line and broad (±1/2↔±3/2) satellites displaying first-order quadrupole splitting. This has recently been demonstrated for the tetrahedrally coordinated [Cu(*t*-BuNC)$_4$]X (X = Cl, Br, I) complexes, for example.[27] For larger ^{65}Cu quadrupole coupling constants, the (±1/2↔±3/2) satellites become too broad to detect, and the central (−1/2↔1/2) line shows a line shape due to second-order quadrupole broadening. At lower values of the static external field strength B_0 (*i.e.* ≤9.4 T), if the ^{65}Cu quadrupole coupling constant C_Q is greater than about 20 MHz, this second-order broadening becomes too great to allow detection of this resonance by a single solid-echo experiment, and frequency-offset subspectral addition methods (sometimes with very large numbers of subspectra) or NQR techniques need to be invoked. This is the case for the compounds [XCu(dptu)$_2$]·H$_2$O (X = Cl, Br, I) studied in the present work, where ^{65}Cu coupling constants of 50 MHz or more were determined from the NQR spectra of these compounds (see below); these large C_Q values are attributed to the distorted trigonal copper(I) coordination environments in these compounds. However, for the dimeric [X$_2$Cu$_2$(dptu)$_4$] compounds, in which the Cu atoms are found in distorted tetrahedral coordination environments, at the lower B_0 fields implemented in this study (*i.e.* ≤9.4 T), the Cu nuclear quadrupole coupling is sufficiently small to be accommodated by a single ^{65}Cu NMR solid-echo measurement, or only a few solid-echo measurements in a summed frequency-offset arrangement.

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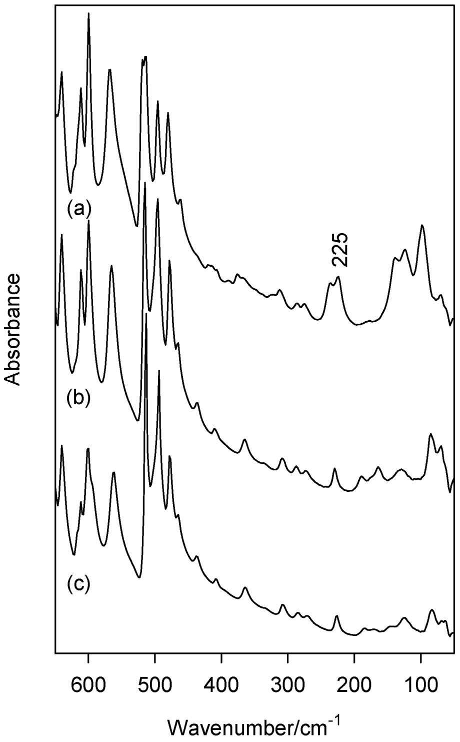

Fig. 5 Far-IR spectra of (a) $[Cl_2Cu_2(dptu)_4]\cdot 2CH_3CN$, and (b, c) $[X_2Cu_2(dptu)_4]$ (X = Br, I).

The broadline static ^{65}Cu NMR spectra acquired at 9.4 and 7.05 T of $[Cl_2Cu_2(dptu)_4]\cdot 2CH_3CN$, and $[X_2Cu_2(dptu)_4]$ (X = Br, I) are shown in Fig. 6, together with simulations of the experimental spectra obtained using the parameters given in Table 5. The broadened lines observed in the spectra are due to the ($-1/2\leftrightarrow 1/2$) transition of the copper nucleus, and the linewidth contains contributions from both the second-order ^{65}Cu nuclear quadrupole interaction and the ^{65}Cu chemical shift anisotropy. For the field strengths employed in this work the quadrupole interaction is dominant and, since the second-order quadrupole interaction is inversely proportional to the external magnetic field strength B_0,[26b] the lines are narrower at 9.4 T than at 7.05 T (Fig. 6). The quadrupole coupling constants C_Q lie in the range 15–16 MHz, and are much lower than the values observed for the monomeric $[XCu(dptu)_2]$ compounds (50 MHz or greater; see below). This is entirely consistent with the change from trigonal planar to tetrahedral coordination from the monomeric to the dimeric complexes. There is a slight trend of decreasing C_Q with X along the series Cl > Br > I (Table 5). A more pronounced trend in the same direction is observed for the monomeric $[XCu(dptu)_2]$ compounds (see below), and this is discussed further in the next section.

The isotropic chemical shifts δ_{iso} for $[X_2Cu_2(dptu)_4]$ lie in the middle of the range −100 to 1050 ppm that has recently been reported for a range of copper(I) coordination compopunds.[28] In this latter work it was noted that there is no simple correlation between δ_{iso} and the coordination geometry or the chemical nature (*e.g.* electronegativities) of the first coordination sphere atoms. The only noticeable trend was that complexes with phosphine ligands showed smaller shifts (*i.e.* greater shielding) than those without such ligands. The present results for $[X_2Cu_2(dptu)_4]$ are consistent with both of these observations; the δ_{iso} values are higher than those for all of the phosphine ligand complexes previously reported,[28] but other trends are not consistent between different series of compounds. Thus, there are several instances in the phosphine ligand complexes in which change from a more electronegative to a less electronegative halide ligand X (*e.g.* from X = Cl to Br) results in an increase in δ_{iso},[28] but the opposite trend is observed for the present series of $[X_2Cu_2(dptu)_4]$ complexes (Table 5).

$^{63/65}$Cu NQR spectroscopy

The $^{63/65}$Cu NQR frequency ν_Q is related to the nuclear quadrupole coupling parameters by the equation:

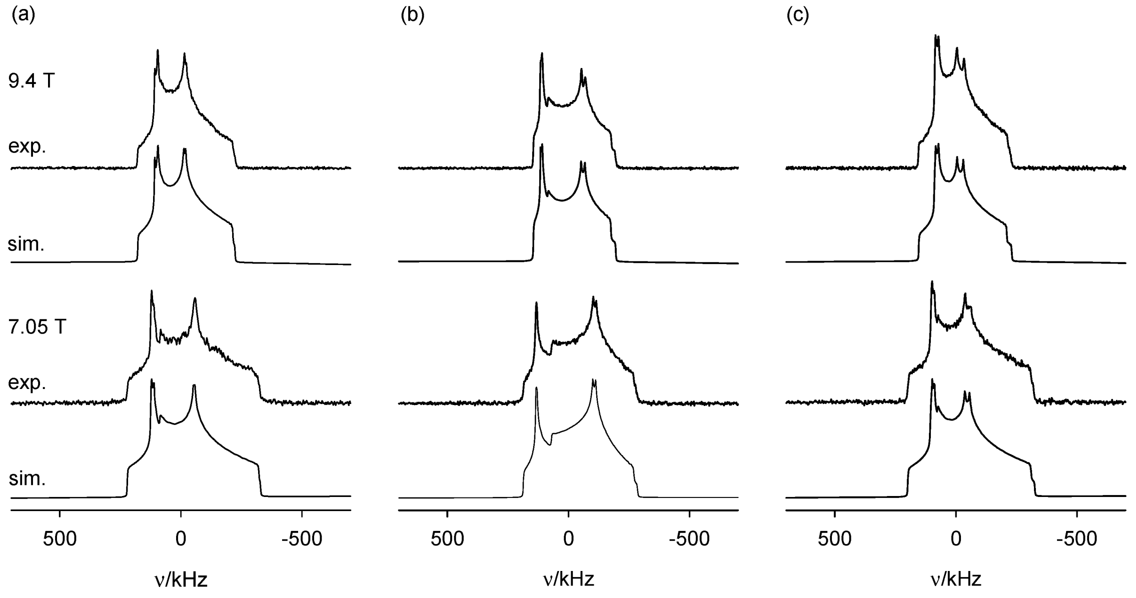

Fig. 6 Broadline static ^{65}Cu NMR spectra at 9.4 and 7.05 T of (a) $[Cl_2Cu_2(dptu)_4]\cdot 2CH_3CN$, and (b, c) $[X_2Cu_2(dptu)_4]$ (X = Br, I) (exp. = experimental spectrum; sim. = simulation using the parameters in Table 5).

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Table 5 ^{65}Cu NMR data for $[Cl_2Cu_2(dptu)_4]\cdot 2CH_3CN$, and $[X_2Cu_2(dptu)_4]$ (X = Br, I)

Compound	δ_{iso} ^{a} (ppm)	C_Q ^{b}/MHz	η_Q ^{b}	Ω^c (ppm)	κ^c	$\Delta\delta^d$ (ppm)	η_δ ^{d}	α, β, γ^e
$[Cl_2Cu_2(dptu)_4]\cdot 2CH_3CN$	505	15.77	0.557	536	0.386	–454	0.544	–20, 174, 36
$[Br_2Cu_2(dptu)_4]$	426	15.62	0.370	594	0.338	–496	0.595	–47, 166, 7
$[I_2Cu_2(dptu)_4]$	367	15.116	0.611	570	0.302	–471	0.634	–17, 164, 47

[a] Relative to Cu(I)Cl; subtract 337.0 ppm to convert to the standard $[Cu(CH_3CN)_4]ClO_4$ chemical shift scale (see Experimental). [b] $C_Q = e^2qQ/h$ is the nuclear quadrupole coupling constant; η_Q is the electric field gradient asymmetry parameter. [c] $\Omega = (\delta_{11} - \delta_{33})$, $\kappa = 3(\delta_{22} - \delta_{iso})/(\delta_{11} - \delta_{33})$, where $\delta_{11} > \delta_{22} > \delta_{33}$. [d] $\Delta\delta = \delta_{33} - 1/2(\delta_{11} + \delta_{22}) = 3/2(\delta_{33} - \delta_{iso})$, $\eta_\delta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso})$, where $|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$. [e] α, β, γ = Euler angles relating the nuclear quadrupole and chemical shift tensor frames.

$$\nu_Q = (1/2)C_Q(1 - \eta_Q{}^2/3)^{1/2} \qquad (2)$$

where C_Q is the nuclear quadrupole coupling constant and η_Q is the electric field gradient asymmetry parameter. This latter parameter ($0 \leq \eta_Q \leq 1$) cannot be determined from the zero-field NQR frequency, but the assumption $\eta_Q = 0$ yields the lower limit of C_Q (the minimum value of $(1 - \eta_Q{}^2/3)^{1/2}$ in eqn (2) is 0.82; the assumption that it is unity involves an 18% error at most). Hence, the NQR frequencies in Table 6 imply ^{65}Cu C_Q values in the approximate range 50–60 MHz, which are much greater than the 15–16 MHz observed for the dimeric $[X_2Cu_2(dptu)_4]$ compounds, as expected for a change from tetrahedral to trigonal planar coordination.

The $^{63/65}$Cu NQR frequencies for $[XCu(dptu)_2]\cdot H_2O$ (X = Cl, Br, I) are compared with those for a number of related compounds in Table 6. The values obtained are very similar to those previously reported for a number of trigonal $[XCu(xetu)_2]$ (X = Cl, Br, I; xetu = *N*-alkylimidazolidine-2-thione (imidazolidine-2-thione ≡ ethylenethiourea, etu)) complexes (Table 6).[13,17–19] Although these studies did not include any complete families $[XCu(xetu)_2]$ with the same xetu ligand in each member of the family, the results indicated that in general the frequencies decrease in the order Cl > Br > I,[17] and this is reflected in the selection of data for such compounds in Table 6. The results for the homologous series of compounds $[XCu(dptu)_2]\cdot H_2O$ confirm this trend (Table 6). A similar trend has been observed in the copper NQR frequencies of CuX and $[CuX_2]^-$ species, and has been shown to be due to an increasing degree of contraction of the Cu 4p orbital that is involved in bonding with the halogen atom, in the order Cl > Br > I.[30,31] The same trend, with presumably the same cause, has been observed in a number of other copper(I) complexes,[32] and the results of the present study provide further evidence of this. In the previously reported studies of the $[XCu(xetu)_2]$ (X = Cl, Br, I) complexes, it was shown that for a given X the copper NQR frequency increases linearly with decreasing S–Cu–S angle.[13] From the close similarity of the substituted imidazolidine-2-thione and thiourea ligands, it might be expected that the present results for the dptu complexes would obey the same relationships, but this in not the case. The S–Cu–S angles in the dptu complexes are considerably smaller than those in the imidazolidine-2-thione complexes, implying that the copper NQR frequencies for the dptu complexes would be higher, but it is clear from the results in Table 6 that this is not the case. Substituting the S–Cu–S angles for the dptu complexes (Table 2) into the empirical relationships established for the imidazolidine-2-thione complexes results in predicted copper NQR frequencies of 35.2 and 29.5 MHz for $[XCu(dptu)_2]\cdot H_2O$ (X = Cl, Br), which are clearly well above the observed values. This relationship is therefore clearly not of wide applicability to $[XCuL_2]$ complexes in which L is a general thiourea-like ligand.

Table 6 Copper NQR frequencies for $[XCu(dptu)_2]\cdot H_2O$ (X = Cl, Br, I) and related compounds

	ν_Q/MHz	
Compound^a	^{63}Cu	^{65}Cu
$[ClCu(dptu)_2]\cdot H_2O$ ^{b}	28.42	26.30
$[BrCu(dptu)_2]\cdot H_2O$ ^{b}	27.31	25.27
$[ICu(dptu)_2]\cdot H_2O$ ^{b}	25.90	23.96
$[ClCu(metu)_2]$ ^{c}	29.481	
$[ClCu(eetu)_2]$ ^{c}	28.802	
$[ClCu(petu)_2]$ ^{c}	28.388	
$[ClCu(ipetu)_2]$ ^{c}	30.021	
$[BrCu(eetu)_2]$ ^{c}	27.756	
$[BrCu(ipetu)_2]$ ^{c}	28.730	
$[ICu(petu)_2]$ ^{c}	26.068	
$[Cu(tmtu)_3]BF_4$ ^{d}	27.390	25.341
$[Cu(tmtu)_3]ClO_4$ ^{d}	27.390	25.340

[a] Ligand abbreviations: xetu as in Table 3, tmtu = tetramethylthiourea. [b] This work, $T \approx 290$ K. [c] Ref. 13, $T = 298$ K. [d] Ref. 29, $T = 296$ K.

The copper NQR frequencies for $[XCu(dptu)_2]\cdot H_2O$ are very similar to those for $[Cu(tmtu)_3]X$ (tmtu = tetramethylthiourea; X = BF_4, ClO_4; Table 6).[29]

Conclusion

The CuX/dptu (1 : 2) system yields two homologous series of compounds that contain isostructural monomeric $[XCu(dptu)_2]$ and dimeric $[(dptu)XCu(\mu\text{-}S\text{-}dptu)_2CuX(dptu)]$ complexes. These provide a basis for investigating the relationship between the structures and the spectroscopic properties of these compounds. In particular, measurement of the ^{63,65}Cu NQR and ^{65}Cu NMR spectra of the monomeric and dimeric complexes has allowed for the first time an investigation of the change in copper nuclear quadrupole coupling with change in coordination geometry and change in the halide ligand. The results demonstrate the utility of ^{65}Cu NMR spectroscopy for the characterization of copper(I) complexes in distorted tetrahedral coordination environments.

Acknowledgements

We are grateful to AINSE (Grants No. 02190, 03011) for financial assistance. Support from the Thailand Research Fund (Grant No. RTA 4880008) is gratefully acknowledged.

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