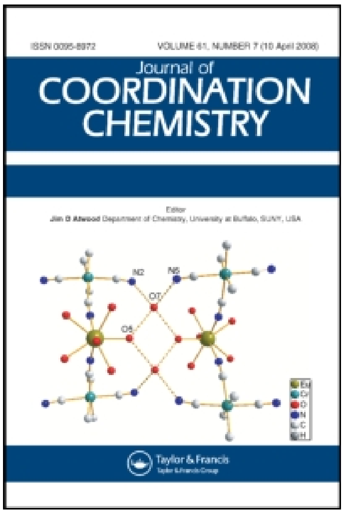

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, Crystal Structure and Characterization of Polynuclear Potassium(I), Copper(II) and Cobalt(II) Complex with Acetylacetonethylenediamine

Liang Shen[a]; Guoding Sheng[a]; Jin Qiu[a]; Yijian Zhang[a]
[a] Department of Chemistry, Hangzhou Teachers College, Hangzhou, P.R. China

To cite this Article Shen, Liang , Sheng, Guoding , Qiu, Jin and Zhang, Yijian(2003) 'Synthesis, Crystal Structure and Characterization of Polynuclear Potassium(I), Copper(II) and Cobalt(II) Complex with Acetylacetonethylenediamine', Journal of Coordination Chemistry, 56: 7, 603 — 610

To link to this Article: DOI: 10.1080/0095897031000110655

URL: http://dx.doi.org/10.1080/0095897031000110655

J. Coord. Chem., Vol. 56, No. 7, 10 May 2003, pp. 603–610

Taylor & Francis
Taylor & Francis Group

SYNTHESIS, CRYSTAL STRUCTURE AND CHARACTERIZATION OF POLYNUCLEAR POTASSIUM(I), COPPER(II) AND COBALT(II) COMPLEX WITH ACETYLACETONETHYLENEDIAMINE

LIANG SHEN*, GUODING SHENG, JIN QIU and YIJIAN ZHANG

Department of Chemistry, Hangzhou Teachers College, Hangzhou 310012, P.R. China

(Received 2 June 2002; Revised 20 August 2002; In final form 5 February 2003)

The title complex $[K\{Cu(acen)\}_3]_2[Co(NCS)_4]\cdot 1/4CH_3OH$ (acen = acetylacetonethylenediamine anion) has been prepared and characterized. Single-crystal x-ray analysis reveals that the complex crystallizes in space group $P1$ with $a = 11.442(2)$, $b = 15.098(3)$, $c = 28.500(4)$ Å, $\alpha = 82.77(1)$, $\beta = 83.58(1)$, $\gamma = 85.07(1)°$. The crystal consists of the complex $[K\{Cu(acen)\}_3]^+$ cations, $[Co(NCS)_4]^{2-}$ anions and methanol molecules. Three [Cu(acen)] molecules function as bridging ligands through phenolic O atoms to one K^+ to give the tetranuclear $[K\{Cu(acen)\}_3]^+$ cation. Each copper(II) atom in the cation is in a square-planar geometry, being coordinated by two oxygen atoms and two nitrogen atoms from a quadridentate acen ligand. The cobalt(II) atom is coordinated by four nitrogen atoms of thiocyanate ligands, forming a deformed tetrahedral environment. The IR and UV–Vis spectra have also been investigated.

Keywords: Copper(II); Cobalt(II); Acen; Polynuclear complex; Crystal structure

INTRODUCTION

Multinuclear metal complexes are of great interest not only in elucidating the magnetic coupling between metal ions [1,2], but also in model compounds of the active sites of multi-metalloenzymes [3,4]. For the synthesis of hetero-metal polynuclear complexes, two synthetic methods have been employed. One is the method that uses a polynucleating ligand exhibiting multi-inequivalent coordination sites. The other is the method that uses a "ligand complex" which involves coordination ability to other metal ions. The latter method has advantages for syntheses of hetero-metal complexes with the systematic combination of metal ions and homo-metal complexes with inequivalent coordination geometries. A few "ligand complexes" are known. *N*,*N*′-ethylenebis (salicylideneaminato)copper(II) or zinc(II) (hereafter abbreviated as [Cu(salen)] or [Zn(salen)]) and derivatives can act as electrically neutral bidentate "ligand complexes" through the μ-phenoxo bridge [5,6]. Because of similar structures, divalent transition

---

*Corresponding author. E-mail: shenchem@sina.com

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897031000110655

metal complexes with acetylacetonethylenediamine (abbreviated as [M(acen)] (M=Cu, Ni, Co) can be "ligand complexes". In this article, we report the synthesis, crystal structure and characterization of a potassium(I), copper(II) and cobalt(II) polynuclear complex by use the neutral ligand complex [Cu(acen)].

EXPERIMENTAL

Preparation

[Cu(acen)] and $K_2[Co(NCS)_4]$ were prepared by literature procedure [7,8]. To a methanol solution (15 mL) of [Cu(acen)] (2 mmol, 560 mg) was added a methanol solution of $K_2Co(NCS)_4$ (1 mmol, 440 mg) with stirring. The resulting solution was allowed to stand at room temperature; three days later dark blue prism crystals suitable for single-crystal X-ray determination were formed. C, H and N analysis with an Erba 1160 instrument supported the composition $[K\{Cu(acen)\}_3]_2[Co(NCS)_4] \cdot 1/4CH_3OH$. Anal. Calcd. for $C_{76.25}H_{109}N_{16}O_{12.25}S_4CoCu_6K_2$(%): C, 43.74; H, 5.21; N, 10.71. Found: C, 43.68; H, 5.43; N, 10.98. Infrared spectra were recorded using a Nicolet 205 Spectrophotometer (4000–400 cm^{-1}) with a crystalline sample spread on KBr pellets. Electronic spectra were measured in methanol by using a Shimadzu UV-260 spectrophotometer.

Crystal Structure Determination

A single crystal with dimensions $0.48 \times 0.46 \times 0.28$ mm was mounted on a glass fiber and used for the structure determination. Diffraction intensity data were collected on a Siemens P4 diffractometer up to $(2\theta)_{max}$ of 50.0 with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω scan technique. A total of 16986 independent reflections were collected, among which 9068 reflections were considered as observed $[I > 2\sigma(I)]$ and used for the structure refinement. Usual Lp and empirical absorption corrections were applied.

The structure was solved by direct methods followed by Fourier synthesis. The structure was refined on F^2 by full-matrix least-squares methods. Hydrogen atoms were generated geometrically and allowed to ride on their parent carbon and nitrogen atoms. The carbon atoms of C(6) and C(7), C(30) and C(31), C(66) and C(67) were disordered over two orientations. Anisotropic refinement including all non-H atoms, using the SHELXTL software package [9], converged to agreement factors $R = 0.0417$ and $R_w = 0.0990$, where $w = 1/[\sigma^2(F_o^2) + (0.0568P)^2]$. The highest peak in the final difference Fourier map was 0.658 e Å^{-3}. Atomic scattering factors used were taken from International Tables for X-ray crystallography [10].

RESULTS AND DISCUSSION

Crystal Structure

Crystal data: $C_{76.25}H_{109}N_{16}O_{12.25}S_4CoCu_6K_2$, M = 2092.40, triclinic, space group $P\bar{1}$, $a = 11.442(2)$, $b = 15.098(3)$, $c = 28.500(4)$ Å, $\alpha = 82.77(1)$, $\beta = 83.58(1)$, $\gamma = 85.07(1)°$, $V = 4840.7(2)$ Å^3, $Z = 2$, $D_c = 1.436\ g\,cm^{-3}$, $F(000) = 2159$, μ(Mo-Kα) = 1.693 mm^{-1}.

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

Atom	*X*	*Y*	*Z*	U_{eq}
Cu(1)	448(1)	1256(1)	4908(1)	53(1)
Cu(2)	5193(1)	2080(1)	1913(1)	60(1)
Cu(3)	5256(1)	2632(1)	3232(1)	58(1)
Cu(4)	7136(1)	1246(1)	−108(1)	60(1)
Cu(5)	1314(1)	3682(1)	5066(1)	58(1)
Cu(6)	9619(1)	3555(1)	101(1)	70(1)
Co	2054(1)	7371(1)	2592(1)	92(1)
K(1)	2591(1)	2414(1)	4115(1)	61(1)
K(2)	7432(1)	2292(1)	901(1)	69(1)
S(1)	4389(2)	7700(1)	3785(1)	108(1)
S(2)	−403(1)	5010(1)	2730(1)	104(1)
S(3)	686(2)	10306(1)	2072(1)	114(1)
S(4)	5288(2)	6853(1)	1477(1)	143(1)
O(1)	881(2)	1223(2)	4235(1)	61(1)
O(2)	2093(2)	1348(2)	4956(1)	65(1)
O(3)	6531(2)	1330(2)	1701(1)	64(1)
O(4)	5997(3)	3043(2)	1558(1)	86(1)
O(5)	4534(2)	1686(2)	3635(1)	65(1)
O(6)	3849(3)	3346(2)	3385(1)	68(1)
O(7)	8395(3)	1140(2)	296(1)	67(1)
O(8)	6046(3)	1410(2)	443(1)	63(1)
O(9)	2857(2)	3594(2)	4723(1)	62(1)
O(10)	724(3)	3451(2)	4491(1)	68(1)
O(11)	9348(3)	3240(2)	774(1)	78(1)
O(12)	7956(3)	3492(2)	81(1)	76(1)
O(13)	7142(16)	−2114(14)	2895(9)	237(18)
N(1)	−1197(3)	1143(2)	4859(1)	54(1)
N(2)	−15(3)	1333(2)	5574(1)	62(1)
N(3)	4346(3)	1110(3)	2249(1)	66(1)
N(4)	3834(3)	2845(3)	2109(1)	69(1)
N(5)	6590(3)	1878(3)	3010(1)	68(1)
N(6)	6076(4)	3614(3)	2900(2)	73(1)
N(7)	8178(4)	1347(3)	−682(1)	69(1)
N(8)	5890(4)	1138(3)	−503(1)	65(1)
N(9)	1900(4)	3926(2)	5639(1)	64(1)
N(10)	−235(3)	3827(2)	5401(2)	63(1)
N(11)	11270(4)	3699(3)	121(2)	77(1)
N(12)	9938(5)	3861(3)	−570(2)	85(1)
N(13)	2795(5)	7446(4)	3169(2)	106(2)
N(14)	935(5)	6432(4)	2680(2)	103(2)
N(15)	1284(5)	8539(4)	2398(2)	96(2)
N(16)	3347(5)	7077(4)	2109(2)	106(2)
C(1)	743(5)	1089(4)	3436(2)	100(2)
C(2)	152(4)	1105(3)	3933(2)	61(1)
C(3)	−1007(4)	1012(3)	4033(2)	66(1)
C(4)	−1679(4)	1066(3)	4478(2)	62(1)
C(5)	−2999(4)	1047(4)	4491(2)	100(2)
C(6)	−1910(19)	1045(9)	5331(5)	62(5)
C(7)	−1300(5)	1446(13)	5688(9)	76(7)
C(8)	220(5)	1409(4)	6413(2)	106(2)
C(9)	701(6)	1394(3)	5894(2)	74(2)
C(10)	1925(5)	1429(3)	5782(2)	77(2)
C(11)	2546(4)	1407(3)	5340(2)	68(1)
C(12)	3865(4)	1436(4)	5281(2)	91(2)
C(13)	7675(4)	34(4)	1510(2)	88(2)
C(14)	6576(4)	462(4)	1746(2)	66(1)
C(15)	5724(5)	−44(3)	2000(2)	76(2)
C(16)	4668(5)	274(4)	2258(2)	75(2)
C(17)	3955(5)	−453(4)	2549(2)	114(2)

(*Continued*)

TABLE I Continued

Atom	*X*	*Y*	*Z*	U_{eq}
C(18)	3291(5)	1430(5)	2539(2)	97(2)
C(19)	2886(5)	2325(4)	2343(2)	97(2)
C(20)	2550(5)	4220(4)	2153(2)	109(2)
C(21)	3693(4)	3705(4)	2000(2)	73(2)
C(22)	4581(5)	4205(4)	1728(2)	80(2)
C(23)	5610(5)	3876(4)	1524(2)	86(2)
C(24)	6405(6)	4508(4)	1209(2)	146(3)
C(25)	4059(5)	224(3)	3955(2)	92(2)
C(26)	4848(4)	836(4)	3638(2)	63(1)
C(27)	5812(4)	503(4)	3381(2)	73(1)
C(28)	6672(4)	1006(5)	3079(2)	74(2)
C(29)	7708(4)	458(4)	2543(2)	106(2)
C(30)	7453(8)	2350(7)	2670(3)	83(4)
C(31)	7313(5)	3312(8)	2769(4)	92(4)
C(32)	6369(5)	5184(4)	2559(2)	129(3)
C(33)	5644(6)	4442(5)	2841(2)	82(2)
C(34)	4521(5)	4727(4)	3020(2)	83(2)
C(35)	3699(5)	4206(4)	3275(2)	75(2)
C(36)	2507(5)	4209(4)	3442(2)	112(2)
C(37)	10314(4)	1041(4)	524(2)	89(2)
C(38)	9499(4)	1182(3)	142(2)	66(1)
C(39)	9938(4)	1351(3)	−324(2)	78(2)
C(40)	9295(5)	1451(3)	−722(2)	70(1)
C(41)	9967(5)	1637(4)	−1205(2)	108(2)
C(42)	7505(5)	1461(4)	−1105(2)	86(2)
C(43)	6401(5)	967(4)	−979(2)	85(2)
C(44)	3932(5)	951(4)	−716(2)	88(2)
C(45)	4772(5)	1130(3)	−373(2)	68(1)
C(46)	4307(4)	1279(3)	93(2)	69(1)
C(47)	4914(4)	1403(3)	455(2)	60(1)
C(48)	4262(4)	1539(4)	932(2)	78(2)
C(49)	4897(4)	3716(4)	4520(2)	91(2)
C(50)	3813(4)	3791(3)	4878(2)	67(1)
C(51)	3898(4)	4025(3)	5321(2)	74(2)
C(52)	2971(5)	4059(3)	5697(2)	71(1)
C(53)	3339(5)	4265(4)	6162(2)	102(2)
C(54)	975(5)	3881(4)	6045(2)	89(2)
C(55)	−197(5)	4084(4)	5877(2)	87(2)
C(56)	−2403(4)	4041(4)	5512(2)	102(2)
C(57)	−1226(5)	3833(3)	5217(2)	71(2)
C(58)	−1297(4)	3676(3)	4744(2)	74(2)
C(59)	−381(5)	3515(3)	4419(2)	67(1)
C(60)	−617(5)	3414(4)	3916(2)	87(2)
C(61)	9674(5)	2913(5)	1587(2)	133(3)
C(62)	1013(5)	3208(4)	1068(2)	84(2)
C(63)	1127(5)	3405(4)	954(2)	93(2)
C(64)	11817(4)	3641(4)	494(2)	81(2)
C(65)	13099(4)	3821(4)	466(3)	118(2)
C(66)	11860(20)	4071(11)	−336(4)	108(7)
C(67)	11207(8)	3827(13)	−730(9)	118(6)
C(68)	9519(6)	4196(5)	−1409(2)	148(3)
C(69)	9185(7)	3956(4)	−872(2)	96(2)
C(70)	7967(6)	3868(4)	−749(2)	97(2)
C(71)	7424(5)	3657(3)	−298(3)	83(2)
C(72)	6116(5)	3600(4)	−213(2)	108(2)
C(73)	3475(5)	7554(4)	3419(2)	76(2)
C(74)	369(5)	5843(4)	2700(2)	81(2)
C(75)	1024(5)	9268(5)	2269(2)	80(2)
C(76)	4167(6)	6984(4)	1849(2)	93(2)
C(77)	7740(19)	−2357(16)	2439(12)	250(30)

TABLE II Bond distances (Å) and angles (°)

Cu(1)–O(1)	1.931(3)	Cu(1)–O(2)	1.921(3)
Cu(1)–N(1)	1.926(3)	Cu(1)–N(2)	1.928(4)
Cu(2)–O(4)	1.906(3)	Cu(2)–O(3)	1.912(3)
Cu(2)–N(4)	1.930(4)	Cu(2)–N(3)	1.920(4)
Cu(3)–O(5)	1.904(3)	Cu(3)–O(6)	1.899(3)
Cu(3)–N(5)	1.921(4)	Cu(3)–N(6)	1.913(4)
Cu(4)–O(8)	1.920(3)	Cu(4)–O(7)	1.926(3)
Cu(4)–N(8)	1.944(4)	Cu(4)–N(7)	1.913(4)
Cu(5)–O(9)	1.922(3)	Cu(5)–O(10)	1.922(4)
Cu(5)–N(9)	1.922(4)	Cu(5)–N(10)	1.925(4)
Cu(6)–O(12)	1.921(3)	Cu(6)–O(11)	1.915(3)
Cu(6)–N(12)	1.911(5)	Cu(6)–N(11)	1.928(4)
Co–N(13)	1.953(5)	Co–N(4)	1.964(5)
Co–N(15)	1.946(6)	Co–N(6)	1.966(6)
K(1)–O(1)	2.735(3)	K(1)–O(2)	2.748(3)
K(1)–O(5)	2.702(3)	K(1)–O(6)	2.704(3)
K(1)–O(9)	2.695(3)	K(1)–O(10)	2.737(3)
K(2)–O(3)	2.698(3)	K(2)–O(4)	2.651(3)
K(2)–O(7)	2.684(3)	K(2)–O(8)	2.696(3)
K(2)–O(11)	2.684(3)	K(2)–O(12)	2.812(4)
C(6)–C(7)	1.509(5)	C(18)–C(19)	1.453(7)
C(30)–C(31)	1.506(5)	C(42)–C(43)	1.508(7)
C(54)–C(55)	1.468(7)	C(66)–C(67)	1.510(5)
S(1)–C(73)	1.604(6)	S(2)–C(74)	1.587(6)
S(3)–C(75)	1.626(7)	S(4)–C(76)	1.586(7)
N(13)–C(73)	1.145(6)	N(14)–C(74)	1.137(6)
N(15)–C(75)	1.141(7)	N(16)–C(76)	1.138(7)
N(1)–Cu(1)–N(2)	85.80(16)	N(1)–Cu(1)–O(1)	93.39(14)
N(1)–Cu(1)–O(2)	179.08(14)	N(2)–Cu(1)–O(1)	177.79(15)
N(2)–Cu(1)–O(2)	94.35(15)	O(1)–Cu(1)–O(2)	86.49(13)
N(3)–Cu(2)–N(4)	85.95(19)	N(3)–Cu(2)–O(3)	94.66(17)
N(3)–Cu(2)–O(4)	177.68(17)	N(4)–Cu(2)–O(3)	178.55(15)
N(4)–Cu(2)–O(4)	93.59(17)	O(3)–Cu(2)–O(4)	85.74(14)
N(5)–Cu(3)–N(6)	86.35(19)	N(5)–Cu(3)–O(5)	94.09(16)
N(5)–Cu(3)–O(6)	172.99(15)	N(6)–Cu(3)–O(5)	172.23(16)
N(6)–Cu(5)–O(6)	94.37(18)	O(5)–Cu(3)–O(6)	86.13(13)
N(7)–Cu(4)–N(8)	86.78(18)	N(7)–Cu(4)–O(7)	93.79(16)
N(7)–Cu(4)–O(8)	168.07(15)	N(8)–Cu(4)–O(7)	170.55(15)
N(8)–Cu(4)–O(8)	93.13(15)	O(7)–Cu(4)–O(8)	88.26(13)
N(9)–Cu(5)–N(10)	86.19(12)	N(9)–Cu(5)–O(9)	93.60(15)
N(9)–Cu(5)–O(10)	179.39(15)	N(10)–Cu(5)–O(9)	177.40(14)
N(10)–Cu(5)–O(10)	93.74(16)	O(9)–Cu(5)–O(10)	86.45(13)
N(11)–Cu(6)–N(12)	85.2(2)	N(11)–Cu(6)–O(11)	93.19(17)
N(11)–Cu(6)–O(12)	176.43(17)	N(12)–Cu(6)–O(11)	178.32(19)
N(12)–Cu(6)–O(12)	94.44(19)	O(11)–Cu(6)–O(12)	87.17(15)
N(13)–Co–N(14)	112.2(2)	N(13)–Co–N(15)	108.3(2)
N(13)–Co–N(16)	105.8(2)	N(14)–Co–N(15)	111.3(2)
N(14)–Co–N(16)	109.3(2)	N(15)–Co–N(16)	109.9(2)
C(73)–N(13)–Co	161.6(5)	C(74)–N(14)–Co	172.9(6)
C(75)–N(15)–Co	168.3(6)	C(76)–N(16)–Co	171.6(6)
N(13)–C(73)–S(1)	177.9(6)	N(14)–C(74)–S(2)	179.1(7)
N(15)–C(75)–S(3)	178.3(6)	N(16)–C(76)–S(4)	178.5(7)

Fractional atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are listed in Table I. Selected bond distances and angles are listed in Table II.

The polynuclear complex consists of two $[K\{Cu(acen)\}_3]^+$ cations and one $[Co(NCS)_4]^{2-}$ anion. As shown in Fig. 1, each copper(II) atom in the cation assumes a square-planar coordination geometry, with two amido nitrogen atoms and two

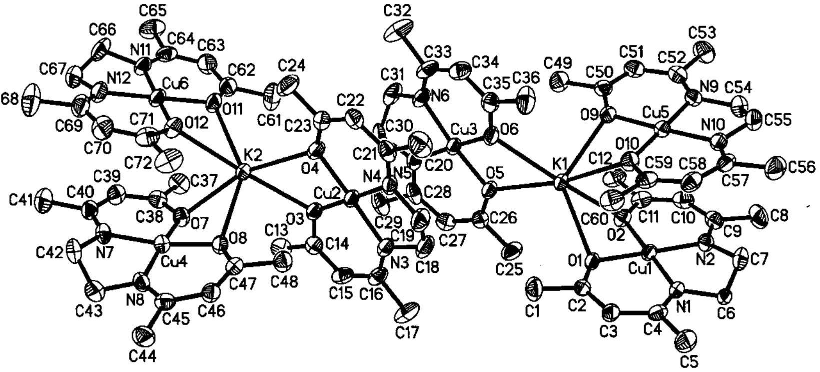

FIGURE 1 An ORTEP view of the $[K\{Cu(acen)\}_3]^+$ cations with atom labels, showing 35% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

oxygen atoms of quadridentate acen ligand. The average bond distances of Cu–O and Cu–N are 1.917(3) and 1.923(4)Å, respectively, which are both shorter than the corresponding distances of [Cu(acen)] [11]. Each potassium ion in the cation is surrounded octahedrally by the six phenolic oxygen atoms from three quadridentate acen ligands. These K–O distances are in the range of 2.651(3)–2.812(4) Å and the values are close to those of 2.672(7)–2.866(9) Å found for $K_2[NiL] \cdot 2DMF \cdot 2H_2O$ (H_4L = 1,2-bis(2-hydroxybenzamido)ethane) [12], 2.682(5)–2.873(5) Å found for $K_2[Cu(hbab)] \cdot 5DMF$ (hbab = 1,2-bis(2-hydrobenzamido)benzene) [13] and consistent with the average distance of 2.8 ± 0.1 Å of potassium crown ether complexes [14]. The most striking feature of the crystal structure is that six phenolic oxygen atoms from three [Cu(acen)] molecules function as μ_2-O bridging ligands to one K^+ to give a tetranuclear $[K\{Cu(acen)\}_3]^+$ cation. This structure feature is different from those observed in other phenolic oxygen bridging complexes [12,13], in which the phenolic oxygen atoms act as μ_3-O bridging ligands to K^+ to give a one-dimensional chain structure.

The cobalt(II) atom in the anion possesses four thiocyanate ligands, each attached to the metal by the nitrogen atom, giving rise to a deformed tetrahedral environment around the cobalt(II) center. The Co–N distances are in the range of 1.946(6)–1.966(6)Å. Co–N–C linkages are bent with angles varying from 161.6(5) to 172.9(6) and N–Co–N angle in the range of 105.8(2)–112.2(2), which are in agreement with the corresponding distances and angles found in $[Cu(cyclam)][Co(NCS)_4]$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) [15]. The thiocyanate groups are almost linear with a mean value of the N–C–S angles of 178.5(6)°. The C–N average distance of 1.140(6) Å and C–S average distance of 1.601(7) Å in the SCN^- moiety show the normal structure of the thiocyanate in the complex.

The C–C distance from 1.468(7) to 1.510(5) Å in the Cu–N–C–C–N ring of the complex is below that expected for a sp^3 hybrid C–C single bond (1.54 Å) [16]. The corresponding C–C bond distance in Cu(acen) [11], $Cu(acen) \cdot 1/2H_2O$ [17], and $Cu(acen) \cdot H_2O$ [18] are 1.55, 1.43, and 1.55 Å, respectively.

Packing diagram of the polynuclear complex as shown in Fig. 2.

Spectroscopic Properties

The infrared spectrum of the complex exhibits a sharp and strong band at 2072 cm^{-1}, which correspond to the $\nu(CN)$ stretching mode of SCN^-, indicating the presence of

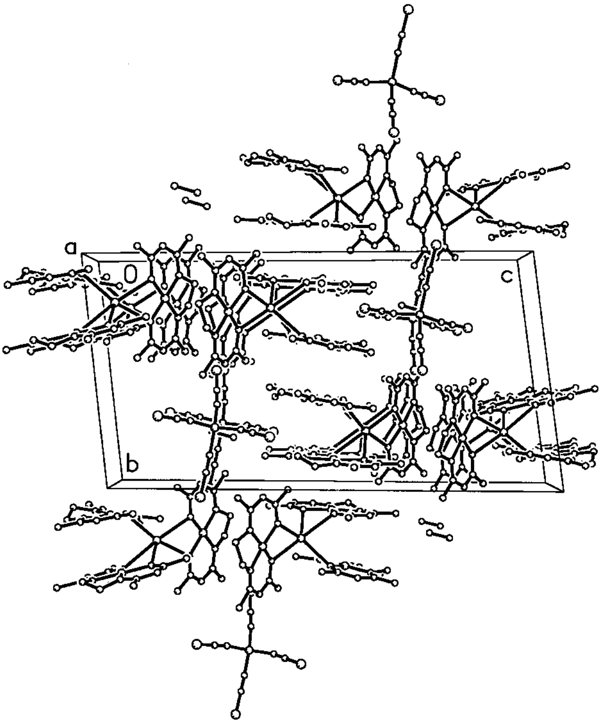

FIGURE 2 Packing diagram of the polynuclear complex.

nitrogen-bonded thiocyanates (Co–NCS) [15]. The weak band corresponding to ν(CS) vibration appears at $870\,\mathrm{cm}^{-1}$, and the δ(NCS) bending mode is observed at $465\,\mathrm{cm}^{-1}$ as a shoulder. The peak at $1605\,\mathrm{cm}^{-1}$ was assigned to the C=N stretching vibration in the complex. Compared with $1640\,\mathrm{cm}^{-1}$ for the C=N stretching vibration of free acen, the $35\,\mathrm{cm}^{-1}$ shift to low wavelength strongly suggests coordination of the Schiff base nitrogen atoms of acen in the complex. The peak at $1530\,\mathrm{cm}^{-1}$ was attributed to a C–O stretching mode in the spectrum of the complex. The shift of the ν(C–O) band to higher frequency compared with that of the "ligand complex" [Cu(acen)] ($1510\,\mathrm{cm}^{-1}$) is the result of an increased constraint of the oxygen atoms due to polynucleation [19].

The reflectance electronic spectrum on the crystalline sample in methanol solvent exhibits a broad absorption at 312 nm and shoulders at 329 and 339 nm. It is reasonable to assign these bands to charge-transfer bands. It is possible that the charge transfer in this case is due to MLCT. At high wavelength the complex shows a broad band centred at 545 nm, which can be assigned to the copper *d–d* transitions.

Supplementary Material

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

References

[1] O. Kahn, Molecular Magnetism (VCH, New York, 1993).
[2] O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science* **49**, 271 (1996).

[3] U. Bossek, T. Weyhermuller, K. Weighardt, B. Nuber and J. Weiss, *J. Am. Chem. Soc.* **6387**, 112 (1990).
[4] Y. Naruta, M. Sasayama and T. Sasaki, *Angew. Chem., Int. Ed. Engl.* **1839**, 33 (1994).
[5] A. Bencini, C. Benelli, A. Caneschi, R.L. Carlin and D. Gatteschi, *J. Am. Chem. Soc.* **8128**, 107 (1985).
[6] L. Shen, D.J. Xu and Y.Z. Xu, *Chinese J. Inorg. Chem.* **806**, 15 (1999).
[7] P.J. Mccarthy, R.J. Hovey, K. Ueno and A.E. Martell, *J. Am. Chem. Soc.* **5820**, 77 (1955).
[8] M.C. Chow and T.C.W. Mak, *Aust. J. Chem.* **1307**, 43 (1992).
[9] Siemens, SHELXTL (version 5.0) (Siemens Industrial Automation Inc. Madison, USA, 1994).
[10] International Tables for X-ray Crystallography, Vol. IV (Kynoch Press, Birmingham, 1974), Present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands.
[11] D. Hall, A.D. Rae and T.N. Waters, *J. Chem. Soc.* 5897 (1963).
[12] Y. Sunatsuki, M. Nakamura, N. Matsumato and F. Kai, *Bull. Chem. Soc. Jpn.* **1851**, 70 (1997).
[13] Y. Sunatsuki, R. Hirata, M. Nakamura, N. Matsumato and F. Kai, *Polyhedron* **4105**, 16 (1997).
[14] P. Hay, J.R. Rustad and C.J. Hostetler, *J. Am. Soc. Chem.* **11158**, 115 (1993).
[15] G. Francese, S. Ferlay, H.W. Schmalle and S. Decurtins, *New J. Chem.* **267**, (1999).
[16] L. Pauling, The Nature of the Chemical Bonds, 3rd Edn. (*Edited by* cornell University Press, Ithaca, New York, 1960), p. 260.
[17] G.R. Clark, D. Hall and T.N. Water, *J. Chem. Soc. A* **233** (1968).
[18] D. Hall, H.J. Morgan and T.N. Waters, *J. Chem. Soc. A* **677** (1966).
[19] D.Z. Liao, Q.H. Zhao and G. L. Wang, *Acta Chimica Sinica* **360**, 48 (1990).