Table 4. *Coordination bond lengths* (Å) *and angles* (°) *for copper*(II)–*cnge complexes*

	Free cnge[a]	Acetate[b]	Nitrate[c]	Chloride[d]	Sulfate[e]
Cu(1)—N(1)	--	2.136	1.92	1.92	1.96
N(1)—C(1)	1.174	1.146	1.16	1.16	1.17
C(1)—N(2)	1.307	1.300	1.29	1.29	1.28
N(2)—C(2)	1.343	1.328	1.33	1.33	1.36
C(2)—N(3)	1.344	1.318	1.34	1.34	1.33
C(2)—N(4)	1.335	1.331	1.31	1.32	1.33
ν_{as}(NCN)	2209 2165	2209 2168	2240 2200	2250 2200	— —

References: (*a*) Hirschfield & Hope (1980); (*b*) $[Cu(OAc)_2(cnge)]_2$, this work; (*c*) $[Cu(cnge)_2(H_2O)_2](NO_3)_2.2H_2O$ (Begley, Hubberstey & Moore, 1985); (*d*) $[Cu(cnge)_2(H_2O)_2Cl_2]$ (Chiesi, Coghi, Mangia, Nardelli & Pelizzi, 1971); (*e*) $[Cu(cnge)(aebg)]SO_4.H_2O$ [aebg = 1-(2-aminoethyl)biguanide] (Coghi, Mangia, Nardelli, Pelizzi & Sozzi, 1968).

orbitals. IR spectroscopy confirms the weakness of the coordination; the ν_{as}(NCN) doublet, which normally shifts from 2209/2165 cm^{-1} for free cnge to higher frequency on coordination to copper(II), is virtually unaltered for $[Cu(OAc)_2(cnge)]_2$ at 2209/2168 cm^{-1} (Table 4). The molecular geometry of the cnge molecule in $[Cu(OAc)_2(cnge)]_2$ does not differ sufficiently from those of the cnge molecules in the other complexes (Table 4) to provide supporting evidence for a different type of interaction. Nonetheless, the bent coordination angle suggests that the interaction might involve *p* orbitals on the nitrile N atom with both σ and π symmetry; the d_{z^2} orbital of the Cu atom exactly bisects these two orbitals.

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Structure of Bis(2,2′-bipyrimidine-*N*,*N*′)dichlorocobalt(II), $[Co(bpm)_2Cl_2]$

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Abstract. $[CoCl_2(C_8H_6N_4)_2]$, $M_r = 446.2$, triclinic, $P\bar{1}$, $a = 8.848\ (2)$, $b = 9.375\ (1)$, $c = 11.906\ (2)$ Å, $\alpha = 74.10\ (1)$, $\beta = 74.36\ (1)$, $\gamma = 83.43\ (1)°$, $V = 913.8\ (3)$ Å^3, $Z = 2$, $D_x = 1.622$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 12.5$ cm^{-1}, $F(000) = 450$, $T = 298$ K, final $R = 0.034$ and $wR = 0.037$ for 3017 reflections with $I > 3\sigma(I)$. The compound consists of neutral $[Co(bpm)_2Cl_2]$ units (bpm = 2,2′-bipyrimidine). Two bidentate bpm ligands and two Cl anions occupying *cis* positions achieve a distorted octahedral environment around the metal ion. The bipyrimidine acts as a bidentate ligand. This compound represents the first structurally characterized example of a bipyrimidine–cobalt(II) mononuclear complex.

Introduction. Compounds of 2,2′-bipyrimidine (bpm) with transition metals have received great attention in the last decade. These complexes were studied for diverse chemical applications such as (*a*) synthetic models for the active site of cytochrome oxidase (Petty, Welch, Wilson, Bottomley & Kadish, 1980), (*b*) photocatalyzed processes (Haim, 1983; Petersen, Murphy, Sahai, Brewer & Ruminski, 1985), and (*c*) interesting magnetic properties (Julve, De Munno, Bruno & Verdaguer, 1988; Julve, Verdaguer, De Munno, Real & Bruno, 1993; De Munno, Julve, Verdaguer & Bruno, 1993).

As a ligand, bpm is very versatile and can give rise to a variety of mono and bimetallic systems, depending on its coordination modes; in fact, it can act as a bis-bidentate (Brewer & Sinn, 1985; Kaim & Kholmann, 1987; Brewer, Murphy & Petersen, 1987; Julve *et al.*, 1988, 1993) or as a bidentate ligand (Matsubayashi, Yamaguchi & Tanaka, 1988; De Munno, Bruno, Julve & Romeo, 1990; Castro, Julve, De Munno, Bruno, Real, Lloret & Faus, 1992; De Munno *et al.*, 1993; Ruminski & Petersen, 1985; Hiskey & Ruminski, 1986). Symmetrical and asymmetrical chelating modes have been observed in both cases.

Mononuclear complexes of bpm were analyzed by X-ray techniques in order to compare their geometries with those of the 2,2′-bipyridine complexes (Morgan, Pennington, Peterson, Ruminski, Bennett & Rommel, 1992; De Munno, Bruno, Dapporto, Julve & Verdaguer, 1988; De Munno *et al.*, 1990, 1993) and they are very interesting as precursors of polymetallic species (G. De Munno & M. Julve, unpublished results). In the present article we report the first crystal structure analysis of a cobalt(II)–bpm mononuclear complex whose synthesis was reported a few years ago (Hiskey & Ruminski, 1986).

Experimental. Orange crystals were obtained by slow diffusion of an ethanolic solution of bpm into an aqueous solution of cobalt(II) chloride. An irregular crystal of $0.12 \times 0.18 \times 0.31$ mm was used for intensity-data collection. Accurate unit-cell dimensions and crystal orientation matrix were obtained from least-squares refinement of 25 strong reflections in the $14 < 2\theta < 30°$ range. Data were collected using a Siemens four-circle diffractometer, ω–2θ scan technique, graphite-monochromated Mo $K\alpha$ radiation and scan range $2\theta = 3$–$54°$ ($0 \le h \le 11$, $-11 \le k \le 11$, $-14 \le l \le 15$). No systematic loss of intensity of two standard reflections ($\bar{3}2\bar{4}$ and 024) was observed during data collection. 4290 reflections were measured (4025 unique, $R_{\rm int} = 0.017$), and Lorentz and polarization corrections were applied to the intensity data. Absorption effects were determined by the ψ-scan method (absorption correction maximum and minimum transmission factors were 0.852 and 0.779, respectively). The structure was solved by standard Patterson methods and subsequently completed by Fourier recycling. 3017 reflections having $I > 3\sigma(I)$ were used to refine 256 parameters by a full-matrix least-squares procedure; the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme used in the last refinement cycles was $w = 1.0000/[\sigma^2(F_o) + 0.000546F_o^2]$. Final $R = 0.034$, $wR = 0.037$, $S = 1.307$, maximum $\Delta/\sigma = 0.017$, maximum and minimum $\Delta\rho$ excursions in ΔF synthesis 0.38 and -0.22 e Å^{-3}, respectively. All non-H atoms were refined anisotropically, while H atoms were placed in calculated positions and refined as riding atoms with free isotropic thermal parameter. Scattering factors for non-H atoms and anomalous-dispersion parameters were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 199), and for H atoms from Stewart, Davidson & Simpson (1965). Solution and refinement were performed with the *SHELXTL-Plus* system (Sheldrick, 1989). The final geometrical calculations were carried out with the *PARST* program (Nardelli, 1983). The graphical manipulations were performed using the *XP* utility of the *SHELXTL-Plus* system.

Discussion. Final atomic coordinates for non-H atoms are listed in Table 1.* Bond distances and angles are given in Table 2. Fig. 1 presents a view of the structure. The compound described is orange–pink, while, according to the previous synthesis, a light pink compound should be obtained (Hiskey & Ruminski, 1986). It is clear that the compound, although with similar formula, contains a different chromophore. Following this hypothesis one can assume that the previous compound would contain two water molecules coordinated to Co$^{\rm II}$ atoms, whereas, in our case, we have obtained the anhydrous form.

The title compound is made up of neutral [$Co(bpm)_2Cl_2$] units in which the metal ion exhibits a distorted octahedral environment. Four N atoms of two bidentate bpm ligands and two Cl anions occupying *cis* positions achieve the octahedral arrangement. This geometry is strictly related to that of the parent 2,2′-bipyridyl complex containing cobalt(II) (Kramer & Strahle, 1986). In fact, distances and angles are in the same range as those previously reported. In both compounds the Co$^{\rm II}$ atoms are in the same geometrical environment. In both, the distortion from a perfect octahedron mainly arises from, apart from the fact that the two Co—Cl distances are significantly greater than the four Co—N distances as expected, the enlargement of the Cl(1)—Co(1)—Cl(2) angle (with respect to the theoretical angle of 90°) and the narrowing of the N(1)—Co(1)—N(6) angle. This behaviour is remarkable for the [$Co(bpm)_2Cl_2$] complex, where

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55854 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1021]

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($\text{Å}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Co(1)	1558 (1)	2175 (1)	2463 (1)	26 (1)
Cl(1)	−876 (1)	990 (1)	3274 (1)	42 (1)
Cl(2)	671 (1)	4685 (1)	1711 (1)	35 (1)
N(1)	3891 (3)	2988 (3)	2052 (2)	30 (1)
C(1)	5030 (3)	3058 (3)	1042 (3)	38 (1)
C(2)	6495 (4)	3525 (4)	928 (3)	47 (1)
C(3)	6744 (4)	3895 (4)	1896 (4)	52 (2)
N(3)	5615 (3)	3867 (3)	2914 (3)	48 (1)
C(4)	4243 (3)	3435 (3)	2926 (3)	32 (1)
C(5)	2917 (3)	3402 (3)	4022 (3)	31 (1)
N(4)	3090 (3)	4079 (3)	4825 (3)	44 (1)
C(6)	1845 (4)	4057 (4)	5766 (3)	47 (1)
C(7)	504 (4)	3356 (4)	5924 (3)	44 (1)
C(8)	450 (4)	2675 (3)	5046 (3)	38 (1)
N(2)	1653 (3)	2719 (3)	4077 (2)	31 (1)
N(5)	1891 (3)	1514 (3)	827 (2)	31 (1)
C(9)	1274 (4)	2239 (4)	−96 (3)	39 (1)
C(10)	1383 (4)	1616 (4)	−1045 (3)	52 (1)
C(11)	2169 (5)	274 (5)	−1013 (3)	57 (2)
N(7)	2815 (4)	−461 (3)	−106 (3)	50 (1)
C(12)	2619 (3)	192 (3)	782 (3)	34 (1)
C(13)	3208 (3)	−612 (3)	1856 (3)	32 (1)
N(8)	4023 (3)	−1889 (3)	1846 (3)	49 (1)
C(14)	4437 (4)	−2579 (4)	2873 (4)	54 (2)
C(15)	4044 (4)	−2034 (4)	3872 (3)	49 (1)
C(16)	3236 (3)	−686 (3)	3777 (3)	39 (1)
N(6)	2822 (3)	40 (3)	2767 (2)	30 (1)

these angles are 100.7 (1) and 82.3°, respectively, while in the $[\mathrm{Co(bpy)_2Cl_2}]$ complex they are 97.9 and 85.8°. Some differences were found in the angles between the bpm rings with respect to the $[\mathrm{Co(bpy)_2Cl_2}]$ complex. These rings are almost planar but they form dihedral angles greater than those previously found in other bpm complexes. In fact, if we consider the angle between the N(1)-C(1)-C(2)-C(3)-N(3)-C(4) plane and the N(2)-C(8)-C(7)-C(6)-N(4)-C(5) plane, which is 12.5 (1)°, we have the largest value found in the bpm monomeric compounds (Morgan *et al.*, 1992; De Munno *et al.*, 1988, 1990, 1993). The second angle formed by the N(5)-C(9)-C(10)-C(11)-N(7)-C(12) and N(6)-C(16)-C(15)-C(14)-N(8)-C(13) planes is 8.8 (1)°. These values are also larger than the corresponding values for the $[\mathrm{Co(bpy)_2Cl_2}]$ complex. The bite angles of the two bpm ligands are 75.8 (1) and 75.4 (1)° and are similar to those found in the $[\mathrm{Co(bpy)_2Cl_2}]$ complex [75.1 (1) and 75.4 (1)°], but they are smaller than those of the $[\mathrm{Cu(bpm)_2(H_2O)}]$ complexes [79.8 (1) for the $\mathrm{ClO_4}$ and 80.1 (1) for the $\mathrm{PF_6}$ derivatives], even though larger distances of the *N*-bpm atoms from the metal centre were found in the $\mathrm{Co^{II}}$ case with respect to the $\mathrm{Cu^{II}}$ case. This behaviour is probably related to the octahedral distortion.

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Table 2. *Bond lengths* (Å) *and interbond angles* (°)

Co(1)—Cl(1)	2.376 (1)	Co(1)—Cl(2)	2.399 (1)
Co(1)—N(1)	2.166 (2)	Co(1)—N(2)	2.143 (3)
Co(1)—N(5)	2.139 (3)	Co(1)—N(6)	2.167 (2)
N(1)—C(1)	1.336 (3)	N(1)—C(4)	1.341 (5)
C(1)—C(2)	1.377 (5)	C(2)—C(3)	1.366 (6)
C(3)—N(3)	1.343 (4)	N(3)—C(4)	1.318 (4)
C(4)—C(5)	1.498 (4)	C(5)—N(4)	1.331 (5)
C(5)—N(2)	1.329 (4)	N(4)—C(6)	1.340 (4)
C(6)—C(7)	1.366 (6)	C(7)—C(8)	1.379 (5)
C(8)—N(2)	1.337 (3)	N(5)—C(9)	1.341 (4)
N(5)—C(12)	1.338 (4)	C(9)—C(10)	1.384 (6)
C(10)—C(11)	1.362 (6)	C(11)—N(7)	1.342 (5)
N(7)—C(12)	1.324 (5)	C(12)—C(13)	1.489 (4)
C(13)—N(8)	1.326 (4)	C(13)—N(6)	1.335 (4)
N(8)—C(14)	1.342 (5)	C(14)—C(15)	1.366 (6)
C(15)—C(16)	1.370 (5)	C(16)—N(6)	1.332 (4)

Cl(1)—Co(1)—Cl(2)	100.7 (1)	Cl(1)—Co(1)—N(1)	168.5 (1)
Cl(2)—Co(1)—N(1)	87.8 (1)	Cl(1)—Co(1)—N(2)	96.5 (1)
Cl(2)—Co(1)—N(2)	89.1 (1)	N(1)—Co(1)—N(2)	75.8 (1)
Cl(1)—Co(1)—N(5)	90.8 (1)	Cl(2)—Co(1)—N(5)	96.4 (1)
N(1)—Co(1)—N(5)	95.9 (1)	N(2)—Co(1)—N(5)	169.9 (1)
Cl(1)—Co(1)—N(6)	90.5 (1)	Cl(2)—Co(1)—N(6)	166.4 (1)
N(1)—Co(1)—N(6)	82.3 (1)	N(2)—Co(1)—N(6)	97.4 (1)
N(5)—Co(1)—N(6)	75.4 (1)	Co(1)—N(1)—C(1)	127.4 (2)
Co(1)—N(1)—C(4)	116.1 (2)	C(1)—N(1)—C(4)	116.4 (3)
N(1)—C(1)—C(2)	121.3 (3)	C(1)—C(2)—C(3)	117.3 (3)
C(2)—C(3)—N(3)	122.9 (3)	C(3)—N(3)—C(4)	115.3 (4)
N(1)—C(4)—N(3)	126.8 (3)	N(1)—C(4)—C(5)	114.8 (3)
N(3)—C(4)—C(5)	118.4 (3)	C(4)—C(5)—N(4)	117.9 (3)
C(4)—C(5)—N(2)	115.7 (3)	N(4)—C(5)—N(2)	126.4 (2)
C(5)—N(4)—C(6)	115.2 (3)	N(4)—C(6)—C(7)	123.1 (4)
C(6)—C(7)—C(8)	117.1 (3)	C(7)—C(8)—N(2)	121.2 (3)
Co(1)—N(2)—C(5)	116.6 (2)	Co(1)—N(2)—C(8)	125.4 (2)
C(5)—N(2)—C(8)	116.9 (3)	Co(1)—N(5)—C(9)	125.0 (2)
Co(1)—N(5)—C(12)	117.1 (2)	C(9)—N(5)—C(12)	117.5 (3)
N(5)—C(9)—C(10)	120.4 (3)	C(9)—C(10)—C(11)	117.5 (3)
C(10)—C(11)—N(7)	123.1 (4)	C(11)—N(7)—C(12)	115.6 (3)
N(5)—C(12)—N(7)	125.9 (3)	N(5)—C(12)—C(13)	115.7 (3)
N(7)—C(12)—C(13)	118.4 (3)	C(12)—C(13)—N(8)	119.0 (3)
C(12)—C(13)—N(6)	115.0 (2)	N(8)—C(13)—N(6)	126.0 (3)
C(13)—N(8)—C(14)	115.2 (3)	N(8)—C(14)—C(15)	123.3 (3)
C(14)—C(15)—C(16)	116.8 (3)	C(15)—C(16)—N(6)	121.5 (3)
Co(1)—N(6)—C(13)	116.6 (2)	Co(1)—N(6)—C(16)	126.3 (2)
C(13)—N(6)—C(16)	117.1 (3)		

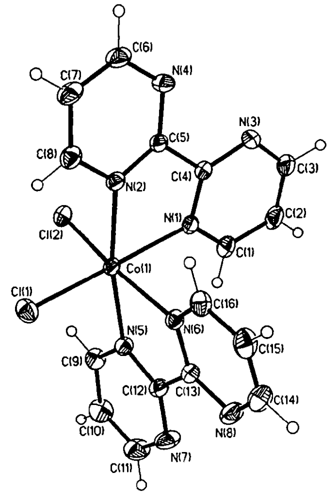

Fig. 1. View of the $[\mathrm{Co(bpm)_2Cl_2}]$ complex, with the atom-numbering scheme.

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A Novel Type of Two-Dimensional Pattern of Association of Mixed-Valence Dimers in the Structures of Two Cation Radical Salts of Thieno- and Selenolo[3,4-*d*]-1,3-dithiol-2-ylidene and a Monovalent Hexanuclear Chalcohalide Rhenium Cluster Anion

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Abstract. 2,2′-Bi(thieno[3,4-*b*]-1,3-dithiol-2-ylidene) nonachloropentathiahexarhenate–dimethylformamide (1/2), $(2C_{10}H_4S_6)^+.Re_6S_5Cl_9^-.2C_3H_7NO$ (1), $M_r = 2375.84$, triclinic, $P\bar{1}$, $a = 9.220$ (5), $b = 11.493$ (2), $c = 12.433$ (3) Å, $\alpha = 102.74$ (2), $\beta = 90.82$ (3), $\gamma = 93.25$ (3)°, $V = 1282$ (6) Å^3, $Z = 1$, $D_x = 3.079$ g cm^{-3}, $F(000) = 1083$, λ(Mo $K\alpha$) = 0.70173 Å, $\mu = 154.9$ cm^{-1}, $T = 293$ K, $R = 0.029$ based on 5662 observed reflections with $I \geq 3\sigma(I)$. 2,2′-Bi(selenolo[3,4-*b*]-1,3-dithiol-2-ylidene) nonachloropentathiahexarhenate–dimethylformamide (1/2), $(2C_{10}H_4S_4Se_2)^+.Re_6S_5Cl_9^-.2C_3H_7NO$ (2), $M_r = 2563.43$, triclinic, $P\bar{1}$, $a = 9.245$ (1), $b = 11.576$ (2), $c = 12.433$ (2) Å, $\alpha = 102.75$ (1), $\beta = 90.72$ (1), $\gamma = 93.21$ (1)°, $V = 1295$ (4) Å^3, $Z = 1$, $D_x = 3.286$ g cm^{-3}, $F(000) = 1155$, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 179.5$ cm^{-1}, $T = 293$ K, $R = 0.026$ based on 4636 observed reflections with $I \geq 3\sigma(I)$. The two compounds are isostructural. Single layers of organic cation radical molecules and inorganic cluster anions alternate along **c** with dimethylformamide (DMF) molecules locked into the lattice *via* a set of C—H···O hydrogen bonds. The compounds are insulating and the organic dimer spins are essentially localized and non-interacting within the organic donor slab which has an unprecedented configuration.

Introduction. A wealth of novel architectures, associated with specific conducting and magnetic properties, has been unravelled for new families of cation radical salts where tetrathiafulvalene and several of its substituted derivatives are associated with large fully inorganic molecular anions (Pénicaud, Boubekeur, Batail, Canadell, Auban-Senzier & Jérome, 1993, and references therein). The present paper describes the structure and magnetic properties of two such salts of organic–inorganic character based on organic donor molecules bearing, on each side, a single exposed chalcogen atom. In contrast to the more commonly used organic donor molecules such as bis(ethylenedithio)tetrathiafulvalene (BEDT-

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