

**(Croconato- $\kappa^2O,O'$ )bis(1,10-phenanthroline- $\kappa^2N,N'$ )cobalt(II), and the nickel(II) and copper(II) analogues**Xia Chen,<sup>a</sup> Hong-Feng Chen,<sup>a</sup> Gang Xue,<sup>b</sup> Hong-Yu Chen,<sup>c</sup>  
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The title complexes,  $[M(C_5O_5)(C_{12}H_8N_2)_2]$ , with  $M = Co^{II}$ ,  $Ni^{II}$  and  $Cu^{II}$ , all lie across twofold rotation axes, around which two 1,10-phenanthroline ligands are arranged in a chiral propeller manner. The  $Co^{II}$  and  $Ni^{II}$  complexes are isostructural, with octahedral coordination geometry, while the local geometry of the  $Cu^{II}$  complex is severely distorted from octahedral.

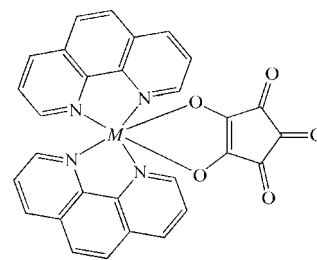
**Comment**

Although the earliest work on croconic acid chemistry dates from 1825 (Gmelin, 1825), croconate coordination chemistry was not developed until the discovery of simple and efficient methods of synthesizing stable croconate salts (Fatiadi *et al.*, 1963). The  $C_5O_5^{2-}$  anion can act both as a terminal bidentate chelate ligand and as a bridging ligand utilizing more than two O atoms for coordination (Chen *et al.*, 2005; Maji *et al.*, 2003; Wang *et al.*, 2002; Sletten *et al.*, 1998).

1,10-Phenanthroline (phen) is a well known neutral bidentate ligand. Probably for steric reasons, many six-coordinate metal-phen complexes contain only two, rather than three, phen ligands, leaving two other sites available for other ligands, such as carbonate, acetate and squarate anions (Niederhoffer *et al.*, 1982; Clifford *et al.*, 1982; Bulut *et al.*, 2004). We report here three metal-phen complexes having bidentate croconate as the second ligand. To our knowledge, there are no previous structure reports on this kind of mixed-ligand complex.

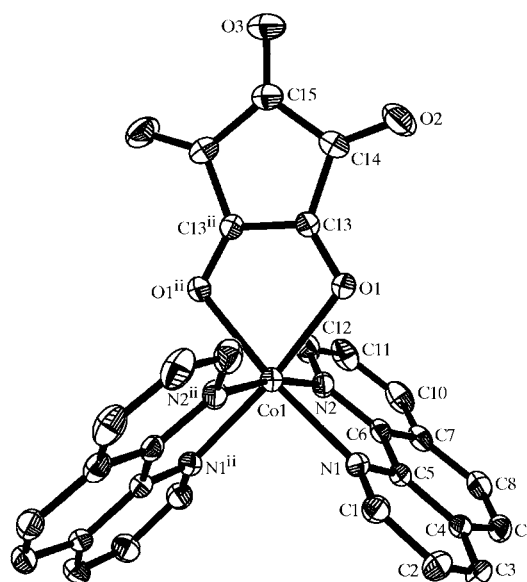
$[Co(C_5O_5)(phen)_2]$ , (I), and  $[Ni(C_5O_5)(phen)_2]$ , (II), are isostructural, but  $[Cu(C_5O_5)(phen)_2]$ , (III), shows distinct differences in comparison with the other two compounds. Each of (I)–(III) lies across a twofold rotation axis, in *Pbcn* for (I) and (II) and in *C2/c* for (III) (Figs. 1–3). Around the twofold axis, two planar phen ligands are arranged in a propeller manner.

We discuss only one of the isostructural pair (I) and (II). In (I), the dihedral angle between the croconate plane and a phen plane is  $86.6(1)^\circ$ , and that between the two phen planes is  $85.7(1)^\circ$ . In (III), the croconate and phen planes are also effectively perpendicular, with a dihedral angle of  $89.7(1)^\circ$ , but the dihedral angle between the two phen planes is only  $40.7(1)^\circ$ . Thus, (I) and (II) adopt regular octahedral coordination, while (III) is severely distorted from octahedral.

(I)  $M = Co$   
(II)  $M = Ni$   
(III)  $M = Cu$ 

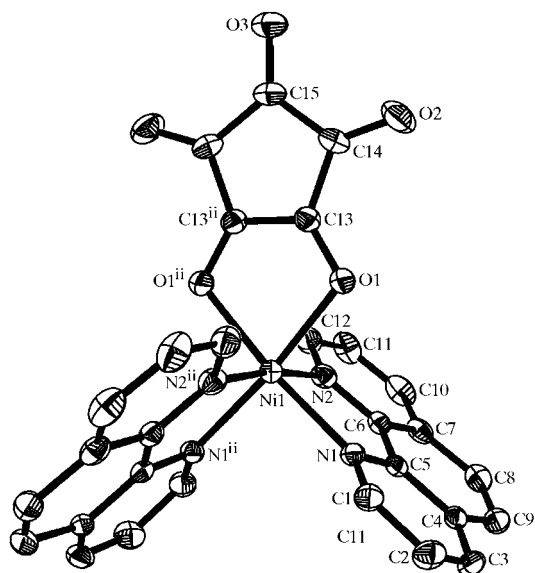
The  $N2-M-N2'$  unit is roughly collinear in all three molecules. The  $N1-Cu-N1^i$  angle [ $126.1(1)^\circ$ ] in (III) is much larger than the  $N1-Co-N1^{ii}$  angle [ $91.3(1)^\circ$ ] in (I) [symmetry codes: (i)  $-x, y, -z + \frac{1}{2}$ ; (ii)  $-x + 1, y, -z + \frac{3}{2}$ ], while the  $O-Cu-O^i$  angle [ $74.9(1)^\circ$ ] in (III) is smaller than the  $O-Co-O^{ii}$  angle [ $81.4(1)^\circ$ ] in (I). Of the metal-ligand bonds (Tables 1–3), the  $Ni-O$  bond is the shortest and the  $Cu-O$  bond the longest. The two types of  $M-N$  bonds show the largest difference in the distorted  $[Cu(C_5O_5)(phen)_2]$ , the  $Cu-N2$  and  $Cu-N1$  bonds being  $1.980(2)$  and  $2.149(2)$  Å, respectively.

All C–O bond lengths of the croconate group are slightly longer than the typical  $Csp^2=O$  length [ $1.208(7)$  Å; Allen *et al.*, 1987], lying in the range  $1.230(5)$ – $1.274(3)$  Å for (I) and

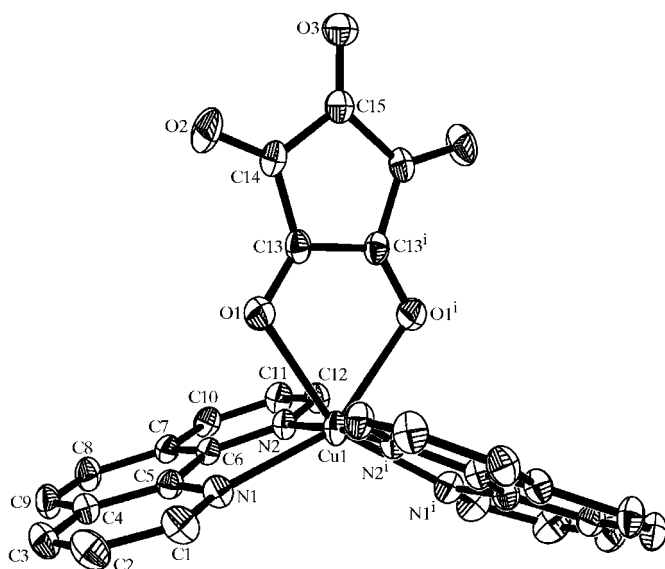


**Figure 1**  
The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted. [Symmetry code: (ii)  $-x + 1, y, -z + \frac{3}{2}$ ]

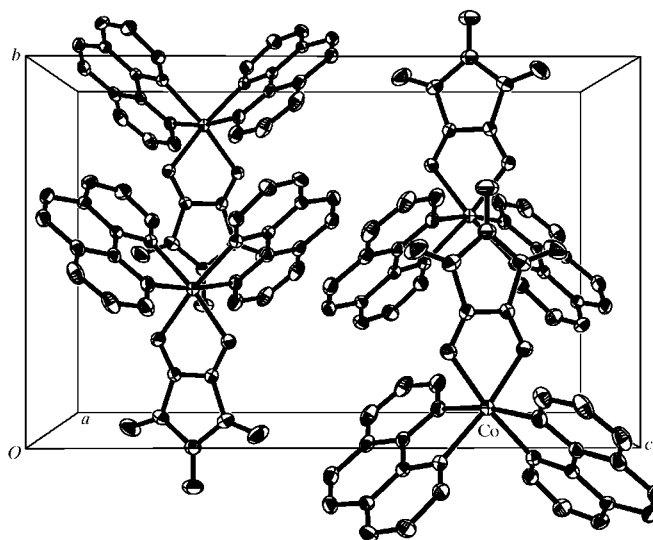
1.229 (5)–1.254 (3) Å for (III) (Tables 1–3). The C–O bond involving the coordinated O atom is the longest. By comparison, the C–O bond lengths of the croconate anion in  $[\text{K}_2(\text{C}_5\text{O}_5)]$  are almost equal, lying in the narrow range 1.241 (2)–1.252 (2) Å (Braga *et al.*, 2002). The variation of the C–C bond lengths in the croconate units shows the same tendency, spanning the ranges 1.435 (5)–1.501 (4) Å in (I) and 1.447 (4)–1.485 (4) Å in (III), but the C–C bond lengths in  $[\text{K}_2(\text{C}_5\text{O}_5)]$  are almost equal (Braga *et al.*, 2002). Compared with the structure of the croconate anion in the  $[\text{K}_2(\text{C}_5\text{O}_5)]$  crystal, the  $\pi$ -conjugation and the fivefold symmetry character



**Figure 2**  
The molecular structure of (II). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted. [Symmetry code: (ii)  $-x + 1, y, -z + \frac{3}{2}$ .]



**Figure 3**  
The molecular structure of (III). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted. [Symmetry code: (i)  $-x, y, -z + \frac{1}{2}$ .]



**Figure 4**  
A packing plot of (I), viewed down the *a* axis. The *a*-axis views of (II) and (III) are similar.

of the coordinated croconate ligand in the three title complexes are relatively weaker.

The molecular twofold axis is along the direction of the molecular dipole moment and the complexes are packed with their dipole moments alternately along the  $+b$  and  $-b$  directions (Fig. 4).

## Experimental

1,10-Phenanthroline (0.10 g),  $[\text{K}_2(\text{C}_5\text{O}_5)]$  (0.11 g), malonic acid (0.10 g) and  $\text{Co}_2(\text{OH})_2(\text{CO}_3)$  (0.10 g) were dissolved in water (15 ml). The mixture was placed in the Teflon liner of an autoclave, which was sealed and heated to 413 K for 96 h, whereupon dark-red prisms of (I) were obtained. 1,10-Phenanthroline (0.10 g),  $[\text{K}_2(\text{C}_5\text{O}_5)]$  (0.11 g), malonic acid (0.10 g) and  $\text{Ni}_2\text{O}_3$  (0.10 g) were dissolved in water (15 ml). The mixture was placed in the Teflon liner of an autoclave, which was sealed and heated to 413 K for 96 h, whereupon brown prisms of (II) were obtained.  $[\text{K}_2(\text{C}_5\text{O}_5)]$  (0.10 g) and  $\text{CuCl}_2$  (0.11 g) were dissolved in a mixed solvent of water (15 ml) and dimethylformamide (10 ml). 1,10-Phenanthroline (0.20 g) was then added. The mixture was heated to 340–350 K under continuous stirring for 20 min and then filtered. Black prisms of (III) were formed by slow evaporation at 313 K.

## Compound (I)

### Crystal data

$[\text{Co}(\text{C}_5\text{O}_5)(\text{C}_{12}\text{H}_8\text{N}_2)_2]$   
 $M_r = 559.39$   
Orthorhombic, *Pbcn*  
 $a = 12.2197$  (10) Å  
 $b = 11.0048$  (11) Å  
 $c = 17.2631$  (14) Å

$V = 2321.5$  (4) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 0.79$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 $0.24 \times 0.20 \times 0.18$  mm

### Data collection

Bruker *P4* diffractometer  
Absorption correction:  $\psi$  scan  
(*XSCANS*; Bruker, 1996)  
 $T_{\min} = 0.779, T_{\max} = 0.869$   
2953 measured reflections  
2283 independent reflections

1413 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.030$   
3 standard reflections  
every 97 reflections  
intensity decay: 1%

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$   
 $wR(F^2) = 0.091$   
 $S = 0.98$   
 2283 reflections

179 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$

**Table 1**

Selected bond lengths (Å) for (I).

C13—O1	1.274 (3)	C15—O3	1.230 (5)
C13—C13 <sup>ii</sup>	1.435 (5)	N1—Co1	2.119 (2)
C13—C14	1.457 (4)	N2—Co1	2.129 (2)
C14—O2	1.232 (4)	O1—Co1	2.120 (2)
C14—C15	1.501 (4)		

Symmetry code: (ii)  $-x + 1, y, -z + \frac{3}{2}$ .

## Compound (II)

### Crystal data

[Ni(C<sub>5</sub>O<sub>5</sub>)(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]  
 $M_r = 559.17$   
 Orthorhombic, *Pbcn*  
 $a = 12.2618 (16) \text{ \AA}$   
 $b = 10.929 (2) \text{ \AA}$   
 $c = 17.171 (3) \text{ \AA}$

$V = 2301.1 (7) \text{ \AA}^3$   
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.90 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 $0.38 \times 0.34 \times 0.18 \text{ mm}$

### Data collection

Bruker *P4* diffractometer  
 Absorption correction:  $\psi$  scan  
 (*XSCANS*; Bruker, 1996)  
 $T_{\min} = 0.775, T_{\max} = 0.854$   
 2872 measured reflections  
 2245 independent reflections

1457 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.041$   
 3 standard reflections  
 every 97 reflections  
 intensity decay: 1%

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$   
 $wR(F^2) = 0.116$   
 $S = 1.04$   
 2245 reflections

179 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$

**Table 2**

Selected bond lengths (Å) for (II).

C13—O1	1.280 (4)	C15—O3	1.229 (6)
C13—C13 <sup>ii</sup>	1.430 (7)	N1—Ni1	2.071 (3)
C13—C14	1.453 (5)	N2—Ni1	2.088 (3)
C14—O2	1.232 (5)	O1—Ni1	2.098 (3)
C14—C15	1.495 (5)		

Symmetry code: (ii)  $-x + 1, y, -z + \frac{3}{2}$ .

## Compound (III)

### Crystal data

[Cu(C<sub>5</sub>O<sub>5</sub>)(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]  
 $M_r = 564.00$   
 Monoclinic, *C2/c*  
 $a = 14.6737 (16) \text{ \AA}$   
 $b = 10.5316 (13) \text{ \AA}$   
 $c = 15.7783 (17) \text{ \AA}$   
 $\beta = 106.666 (9)^\circ$

$V = 2335.9 (5) \text{ \AA}^3$   
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.99 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 $0.30 \times 0.28 \times 0.22 \text{ mm}$

### Data collection

Bruker *P4* diffractometer  
 Absorption correction:  $\psi$  scan  
 (*XSCANS*; Bruker, 1996)  
 $T_{\min} = 0.719, T_{\max} = 0.805$   
 3179 measured reflections  
 2558 independent reflections

1906 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.028$   
 97 standard reflections  
 every 3 reflections  
 intensity decay: 1%

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.088$   
 $S = 1.01$   
 2558 reflections

179 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.41 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$

**Table 3**

Selected geometric parameters (Å, °) for (III).

C13—O1	1.254 (3)	C15—O3	1.229 (5)
C13—C14	1.447 (4)	Cu1—N2	1.9799 (19)
C13—C13 <sup>i</sup>	1.452 (5)	Cu1—N1	2.149 (2)
C14—O2	1.237 (3)	Cu1—O1	2.303 (2)
C14—C15	1.485 (4)		
N2—Cu1—N2 <sup>i</sup>	175.88 (14)	N2 <sup>i</sup> —Cu1—O1	89.12 (8)
N2—Cu1—N1 <sup>i</sup>	97.53 (8)	N1 <sup>i</sup> —Cu1—O1	152.44 (8)
N2—Cu1—N1	80.58 (8)	N1—Cu1—O1	80.37 (8)
N1 <sup>i</sup> —Cu1—N1	126.11 (13)	O1—Cu1—O1 <sup>i</sup>	74.93 (10)
N2—Cu1—O1	94.15 (8)		

Symmetry code: (i)  $-x, y, -z + \frac{1}{2}$ .

All H atoms were positioned geometrically and allowed to ride on their attached atoms [ $C-H = 0.93 \text{ \AA}$  and  $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ ].

For all compounds, data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3090). Services for accessing these data are described at the back of the journal.

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