powder was recrystallized from ethanol and water to give bright colorless crystals, m.p. 570–573 K. Analysis: calculated (mass %) for $C_{21}H_{24}Cl_2N_4O_8Zn$: C 42.30, H 4.05, N 9.33; found: C 42.12, H 4.26, N 9.33.

Crystal data

$[Zn(C_{21}H_{24}N_4)](ClO_4)_2$
M_r = 596.72
Monoclinic
$P2_1/c$
a = 13.398 (3) Å
b = 13.988 (3) Å
c = 13.674 (3) Å
β = 104.24 (2)°
V = 2483.8 (9) Å^3
Z = 4
D_x = 1.596 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 16.72–17.47°
μ = 3.88 mm^{-1}
T = 293 (2) K
Block
0.25 × 0.20 × 0.20 mm
Colorless

Data collection

Rigaku AFC-6*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.396, $T_{\max}$ = 0.460
4001 measured reflections
3819 independent reflections

2850 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.028
$\theta_{\max}$ = 59.49°
$h = -10 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 14$
3 standard reflections every 500 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.184
S = 1.142
3819 reflections
326 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 7.3791P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max}$ = 0.75 e Å^{-3}
$\Delta\rho_{\min}$ = −0.40 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0015 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zn1—N4	1.979 (5)	N1—C3	1.516 (9)
Zn1—N3	1.999 (5)	C34—C33	1.355 (11)
Zn1—N2	1.999 (5)	C34—C35	1.393 (9)
Zn1—N1	2.028 (5)	C5—C6	1.529 (10)
N3—C35	1.327 (8)	C33—C32	1.355 (11)
N3—C31	1.336 (8)	C32—C31	1.390 (9)
N1—C1	1.494 (9)	C31—C6	1.498 (10)
N1—C5	1.503 (8)		
N4—Zn1—N3	119.6 (2)	C5—N1—C3	107.9 (5)
N4—Zn1—N2	114.4 (2)	C33—C34—C35	118.5 (7)
N3—Zn1—N2	111.9 (2)	N1—C5—C6	112.6 (5)
N4—Zn1—N1	102.3 (2)	C32—C33—C34	119.9 (7)
N3—Zn1—N1	102.5 (2)	C33—C32—C31	119.8 (7)
N2—Zn1—N1	103.4 (2)	N3—C31—C32	120.4 (7)
C35—N3—C31	119.6 (5)	N3—C31—C6	118.2 (5)
C35—N3—Zn1	121.8 (4)	C32—C31—C6	121.4 (7)
C31—N3—Zn1	118.2 (4)	N3—C35—C34	121.8 (7)
C1—N1—C5	109.6 (6)	C31—C6—C5	112.7 (6)
C1—N1—C3	109.3 (6)		

H atoms were placed in idealized positions and allowed to ride on their parent atoms with $U_{\rm iso}(H) = 1.2\,U_{\rm eq}(C)$, and C—H = 0.93 and 0.97 Å.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1069). Services for accessing these data are described at the back of the journal.

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A Dinuclear Indium(III) Complex with Two Pyrazolate Bridging Ligands

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Abstract

The crystal structure of bis[μ-3-(2-pyridyl)-1*H*-pyrazolato]-1κ^2N',N^2:2κN^1;1κN^1:2$\kappa N',N^2$-bis[dichloro(dimethylformamide-*O*)indium]–dimethylformamide (1/2), $[In_2Cl_4L_2(dmf)_2]$.2dmf [where H*L* is 3-(2-pyridyl)-pyrazole, $C_8H_7N_3$, and dmf is dimethylformamide,

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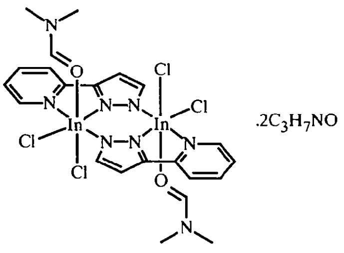
C_3H_7NO], contains pairs of [$InCl_2$(dmf)] fragments linked by two pyrazolate bridges from the deprotonated bridging ligand 3-(2-pyridyl)pyrazolate (L^-). This ligand acts as a bidentate *N*-donor chelate to one metal centre using the pyridyl N and pyrazolyl N^2 atoms, and bridges to the other metal using the (deprotonated) pyrazolyl N^1 atom. Each In^{III} centre, therefore, has an N_3Cl_2O donor set.

Comment

We have been interested recently in the coordination behaviour of the simple ligand 3-(2-pyridyl)-1*H*-pyrazole. In its neutral form with the proton retained at the pyrazolyl N^1 position, this ligand behaves as a simple bidentate chelate. However, deprotonation of the pyrazolyl ring usually results in the ligand bridging two metal centres, and some surprisingly complicated high-nuclearity complexes can be formed (Jones *et al.*, 1997; Jeffery *et al.*, 1997). We were therefore interested to see whether this type of behaviour extends to *p*-block elements.

Reaction of the potentially bridging ligand 3-(2-pyridyl)-1*H*-pyrazole (H*L*) with indium(III) chloride followed by crystallization from dimethylformamide–ether afforded the title compound, (I), in good yield. The crystal structure (Fig. 1) shows that the complex is dinuclear with approximate octahedral coordination geometry about the metal centres, and that it has crystallographically imposed inversion symmetry. Each In^{III} centre is coordinated by the bidentate *N*-donor pocket of one ligand [pyridyl N and pyrazolyl N^2 atoms, N21 and N11 according to the crystallographic numbering scheme; bite angle N11—In1—N21 73.36 (8)°], the deprotonated pyrazolyl N^1 atom (N12^i), two chloride ions and one *O*-donor dmf molecule. The In—N11 and In—N12^i bond distances differ slightly at 2.223 (2) and 2.193 (2) Å, respectively.



(I)

This structure type is rare; the only other crystal structure of a compound with pyrazolate bridges between two In^{III} centres is $(Me_2In)_2(\mu\text{-pz})_2$, in which two deprotonated pyrazolate (pz) anions bridge two tetrahedral In^{III} centres giving a non-planar boat-shaped $In_2(\mu\text{-pz})_2$ core (Hausen *et al.*, 1992). In contrast, the $In_2(\mu\text{-pz})_2$ core of [$In_2Cl_4L_2$(dmf)$_2$] is essentially planar.

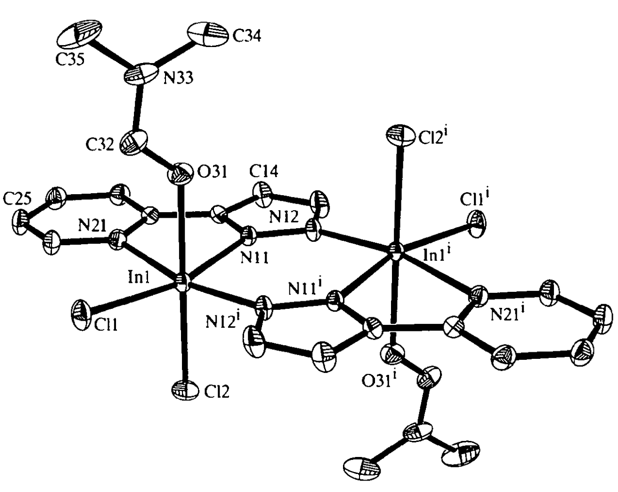


Fig. 1. The structure of the [$In_2Cl_4L_2$(dmf)$_2$] complex in [$In_2Cl_4L_2$(dmf)$_2$].2dmf showing the atomic labelling scheme and 40% probability ellipsoids for non-H atoms.

A comparison of the C—O bond distances in the free lattice dmf molecule [O41—C42 1.204 (4) Å] and the coordinated dmf molecule [O31—C32 1.245 (3) Å] reflects the fact that in the coordinated dmf molecule, the tautomeric form with a single C—O bond and a negative charge on the O atom will be stabilized by coordination to a 3+ metal centre (Bardwell *et al.*, 1995).

Experimental

Mixing equimolar amounts of H*L* and $InCl_3$ in MeOH at room temperature afforded a white precipitate which was collected by filtration and dried. Recrystallization by diffusion of diethyl ether vapour into a concentrated dimethylformamide solution of the product afforded X-ray quality crystals of [$In_2Cl_4L_2$(dmf)$_2$].2dmf. A sample for analysis was dried under vacuum. Found: C 32.4, H 3.5, N 13.5%; required for [$In_2Cl_4L_2$(dmf)$_2$]: C 32.8, H 3.2, N 13.9%. FAB mass spectrum: m/z = 623, $\{In_2Cl_3L_2\}^+$. A suitable crystal was coated with hydrocarbon oil and mounted on a glass fibre at 173 K.

Crystal data

[$In_2Cl_4(C_8H_6N_3)_2$-
($C_3H_7NO)_2$].2C_3H_7NO
M_r = 952.14
Monoclinic
$C2/c$
a = 19.639 (3) Å
b = 13.143 (2) Å
c = 15.1992 (14) Å
β = 101.845 (13)°
V = 3839.6 (9) Å^3
Z = 4
D_x = 1.647 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 340
reflections
θ = 2.0–27.5°
μ = 1.526 mm^{-1}
T = 173 (2) K
Needle
0.40 × 0.22 × 0.09 mm
Colourless

Data collection

Siemens SMART area-detector diffractometer
ω rotation scans with narrow frames
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.53$, $T_{\max} = 0.87$
12 182 measured reflections
4394 independent reflections
3485 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.030$
$\theta_{\max} = 27.5°$
$h = -16 \rightarrow 25$
$k = -17 \rightarrow 15$
$l = -19 \rightarrow 19$
Intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.028$
$wR(F^2) = 0.064$
$S = 1.074$
4394 reflections
217 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.003$
$\Delta\rho_{\max} = 0.526$ e Å^{-3}
$\Delta\rho_{\min} = -0.391$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

In1—N12$^{\text{i}}$	2.193 (2)	In1—N21	2.289 (2)
In1—N11	2.223 (2)	In1—Cl1	2.4449 (7)
In1—O31	2.230 (2)	In1—Cl2	2.4591 (8)
N12$^{\text{i}}$—In1—N11	97.38 (8)	O31—In1—Cl1	89.53 (6)
N12$^{\text{i}}$—In1—O31	86.73 (8)	N21—In1—Cl1	94.27 (6)
N11—In1—O31	82.12 (8)	N12$^{\text{i}}$—In1—Cl2	96.68 (7)
N12$^{\text{i}}$—In1—N21	168.38 (8)	N11—In1—Cl2	93.72 (6)
N11—In1—N21	73.36 (8)	O31—In1—Cl2	174.96 (5)
O31—In1—N21	85.07 (8)	N21—In1—Cl2	91.02 (6)
N12$^{\text{i}}$—In1—Cl1	93.88 (6)	Cl1—In1—Cl2	93.94 (3)
N11—In1—Cl1	165.55 (6)	C32—O31—In1	128.8 (2)

Symmetry code: (i) $1 - x, -y, -z$.

Unit-cell dimensions were determined from reflections taken from three sets of 30 frames (at 0.3° steps in ω) each at 20 s exposure. Slightly more than a full hemisphere of reciprocal space was scanned by 0.3° ω steps at $\varphi = 0$, 90 and 180° with the area detector held at $2\theta = -29°$ and each frame exposed for 20 s. The crystal-to-detector distance was 4.94 cm. The absence of crystal decay was established by repeating the initial 50 frames at the end of data collection and analysing the duplicate reflections. The data were corrected empirically for absorption effects (Sheldrick, 1996) and refined by full-matrix least squares on all F^2 data using *SHELXTL* (Siemens, 1995*a*). H atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} value of their attached atom (for aromatic or other sp^2 C atoms) or 1.5 times the U_{iso} value of their attached atom (for all others).

Data collection: *SMART* (Siemens, 1995*b*). Cell refinement: *SAINT* (Siemens, 1995*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1995*a*). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. 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: BM1206). Services for accessing these data are described at the back of the journal.

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Dipotassium (2,2′-Bipyridyl-*N*,*N*′)-tetracyanoferrate(II) 2.5-Hydrate, $K_2[Fe(bpy)(CN)_4].2.5H_2O$

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Abstract

Analysis of the title complex, $K_2[Fe(CN)_4(C_{10}H_8N_2)].2.5H_2O$, shows that the asymmetric unit contains two $[Fe(bpy)(CN)_4]^{2-}$ units, four K^+ ions and five water molecules. There is extensive hydrogen bonding within the structure and, as expected, all hydrogen-bond donors and acceptors are involved in hydrogen bonding, resulting in a complex three-dimensional network. The water molecules and K^+ ions occupy three different channels in the framework created by the packing of the $[Fe(bpy)(CN)_4]^{2-}$ units.

Comment

The spectroscopic and excited-state properties of tetracyano compounds of the type $[Fe(L\text{–}L)(CN)_4]^{2-}$, where *L–L* is a polypyridyl ligand such as 2,2′-bipyridyl (bpy), 1,10-phenanthroline or bipyrimidine, have been studied in detail (Blundell *et al.*, 1989; Burgess *et al.*, 1992;

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