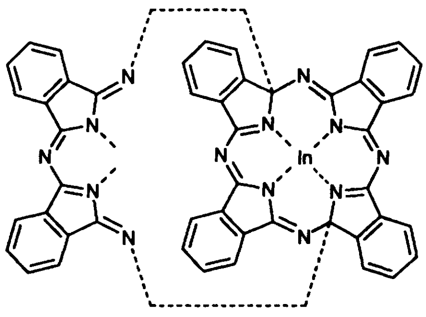
Synthesis and Crystal Structure of an Indium(III) Complex with a Bicyclic Phthalocyanine at 300 K *

Jan Janczak and Ryszard Kubiak
W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 937, 50-950 Wrocław, Poland

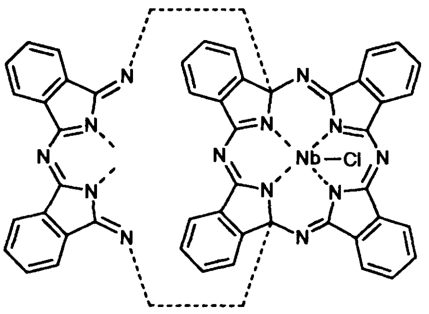
A new green complex of indium(III) [In($C_{48}H_{24}N_{13}$)] has been synthesised in crystalline form from the reaction of indium with 1,2-dicyanobenzene under a low nitrogen pressure at about 210 °C. It crystallizes in the triclinic system, space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions $a = 11.693(2)$, $b = 12.408(3)$, $c = 15.998(4)$ Å, $\alpha = 75.56(3)$, $\beta = 85.63(3)$ and $\gamma = 64.92(3)$°. The structure was solved by Patterson and Fourier-difference methods and refined by block-diagonal least-squares techniques to $R = 0.0707$, $R' = 0.0906$ and $S = 1.85$ for 7128 independent reflections having $F > 4\sigma(F)$ and 560 refined parameters. The molecule consists of an indium(III) cation and hexadentate chelate macrocyclic ligand. The latter is a bicyclic phthalocyaninate composed of six isoindole units forming a distorted trigonal prism with its six N-donor atoms. The conjugation of the π-electron system in the inner 16-membered ring is interrupted by the two sp^3-hybridized bridgehead C atoms. The In–N distances range from 2.203(4) to 2.267(4) Å. The details of the crystal structure are discussed and compared with those of other phthalocyanines.

Metallophthalocyanines have been intensively investigated for their application in the pigment industry and as molecular electrical conductors or semiconductors.[1–6] Among the large number of publications reporting metallophthalocyanines until now few have concerned the crystal structures with trivalent metal ions.[7–14] Several authors[15–21] have reported two coloured compounds (violet-blue and green phthalocyanines with trivalent metal ions) as products formed during the preparation of various lanthanide complexes. Kirin *et al.*[16] identified the violet-blue form as the lanthanide diphthalocyaninate complex Ln(pc)$_2$H (pc = phthalocyaninate, Ln = lanthanide) by elemental analysis. They and also Yamana[22] suggested that the green form was a monophthalocyaninate complex Ln(pc)Cl based upon its optical spectrum compared to those of metal monophthalocyaninates, despite the lack of elemental analysis. It was also suggested[18,20] that both the violet-blue and green forms are metallodiphthalocyanines which would interconvert depending on the nature of the solvent environment and the preparation method.

Recently[23,24] we suggested that the chemical composition of the metallophthalocyanines with trivalent metal ions is strongly dependent on their method of synthesis. We reported[23] the synthesis and crystal structure of the violet triple-decker complex diindium triphthalocyaninate. Subsequently we have slightly modified the preparation method and obtained new green complex compounds in crystalline form with the metals In, Gd, Tl and Ce. Elemental analysis on an energy-dispersive spectrometer and X-ray single-crystal analysis led to the composition and structure of these green complexes as $M^{III}(C_{48}H_{24}N_{13})$.



1



2

Experimental

Synthesis.—Indium filings (0.3 g) and 1,2-dicyanobenzene (0.9 g) were mixed and pressed into pellets. The pellets were inserted into a glass ampoule under nitrogen pressure [about 0.1 atm (*ca.* 10^4 Pa)] and sealed. The ampoule was heated at 210 °C for 1 d which yielded two kinds of good-quality crystals (25 and 5% yields). One kind was identified as [In$_2$(pc)$_3$],[23] the second as [In($C_{48}H_{24}N_{13}$)] (Found: C, 64.30; H, 2.65; In, 12.95; N, 20.05. Calc. for $C_{48}H_{24}InN_{13}$: C, 64.25; H, 2.70; In, 12.80; N, 20.30%).

Crystallography.—A green parallelepiped single crystal of [In($C_{48}H_{24}N_{13}$)] having a mean edge of 0.3 mm was used for data collection on a four-circle KUMA KM-4 diffractometer equipped with a graphite monochromator and Cu-Kα radiation (λ = 1.540 56 Å). Initial examination of the crystal by rotation

---

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

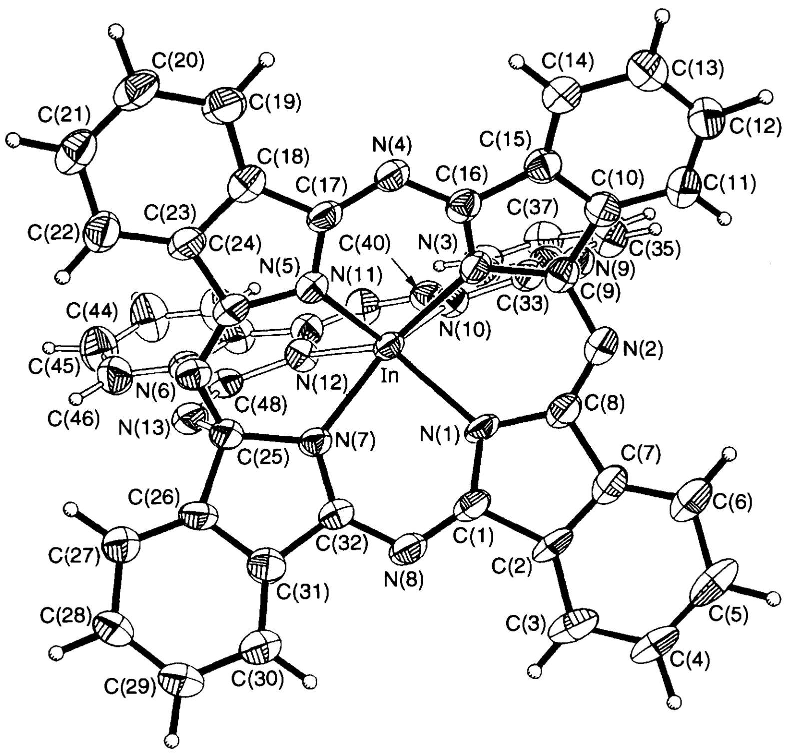


Fig. 1 View of the molecular structure of complex **1** with the atom numbering

and Weissenberg photographs indicated a triclinic system. The unit-cell parameters were refined by least-squares fit of 25 reflections measured in the range 2θ 25–50°. A total of 12 906 reflections was measured in the range $4 < 2\theta < 160°$ [$(\sin\theta/\lambda)_{max} = 0.639$] using the ω–2θ scan technique. Two standard reflections [(044) and (424)] were monitored every 50. They showed no significant intensity variations. Intensities and their standard deviations were corrected for Lorentz and polarization effects. A spherical absorption correction was applied ($\mu R = 0.772$), maximum and minimum transmission factors 0.482 and 0.244, respectively. An empirical secondary extinction correction was applied according to the formula $F_{cor} = F(1 + 0.002\kappa F^2/\sin 2\theta)^{-\frac{1}{4}}$ where κ converged to 0.0087(7). 7817 Independent reflections [7128 with $F > 4\sigma(F)$] were used in the structure solution and refinement.

Structure determination and refinement. The structure was solved by the Patterson heavy-atom method, which revealed the position of the In atom. The remaining atoms were located in successive Fourier-difference synthesis. Initially the structure was refined with isotropic, then anisotropic thermal parameters for all atoms (expected H atoms) by the block-diagonal least-squares method, using the SHELXTL program system.[25] Hydrogen atoms of the phenyl rings were located with geometrical correlation and their thermal parameters fixed ($U_{iso} = 0.07$ Å^2). The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weighting scheme $w = 1/\sigma^2$. The final unweighted and weighted agreement factors converged to $R = 0.0707$ and $R' = 0.0906$. The residual electron density was within +2.78 to −1.93 e Å^{-3}. Scattering factors for neutral atoms and corrections for anomalous dispersion were as in the SHELXTL program system, which was used for all the crystal-structure calculations and drawing. Final agreement factors and crystallographic data are given in Table 1, final positional parameters in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1 Crystallographic data for complex **1**

Formula	$C_{48}H_{24}InN_{13}$
M	897.6
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	11.693(2)
b/Å	12.408(3)
c/Å	15.998(4)
α/°	75.56(3)
β/°	85.63(3)
γ/°	64.92(3)
U/Å^3	2034.7(7)
Z	2
F(000)	904
D_m/g cm^{-3}	1.46 (by flotation)
D_c/g cm^{-3}	1.465
Scan speed/° s^{-1}	0.03–0.12
Scan width/°	1.3 + 0.1 tan θ
h, *k*, *l* ranges	−14 to 14, −14 to 14, −20 to 20
Total reflections	12 906
Unique reflections	7817
Observed reflections [$F > 4\sigma(F)$]	7128
No. parameters	560
Data/parameters	12.73
μ/cm^{-1}	51.46
R	0.0707
R'	0.0906
Goodness of fit	1.85
Mean Δ/σ	0.032

Results and Discussion

The crystal of the complex **1** consists of discrete [In($C_{48}H_{24}N_{13}$)] molecules. A view of the molecule is shown in Fig. 1, which also gives the numbering scheme. Selected bond distances and angles are in Table 3.

The ligand consists of the phthalocyaninate skeleton of four

Table 2 Atomic coordinates (× 10⁴) for complex **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
In	823(2)	4 543(3)	2 612(3)	C(18)	−1 490(4)	4 573(5)	485(4)
N(1)	2 673(3)	4 663(4)	2 489(3)	C(19)	−1 978(5)	4 046(4)	21(4)
N(2)	4 154(4)	2 582(4)	2 406(3)	C(20)	−3 177(6)	4 761(5)	−346(4)
N(3)	1 944(3)	2 911(4)	2 107(3)	C(21)	−3 837(4)	5 979(5)	−322(4)
N(4)	517(4)	2 949(4)	1 074(3)	C(22)	−3 318(4)	6 529(4)	126(4)
N(5)	−362(3)	4 906(4)	1 465(3)	C(23)	−2 142(4)	5 788(4)	528(4)
N(6)	−1 737(4)	7 094(3)	1 232(3)	C(24)	−1 395(4)	6 019(4)	1 108(4)
N(7)	176(4)	6 542(3)	2 142(3)	C(25)	−1 181(4)	7 363(4)	1 879(4)
N(8)	2 057(4)	6 844(4)	2 268(4)	C(26)	−1 171(5)	8 623(4)	1 577(4)
N(9)	3 301(4)	1 433(4)	3 364(4)	C(27)	−2 127(4)	9 747(5)	1 200(5)
N(10)	1 388(4)	2 999(4)	3 824(3)	C(28)	−1 835(5)	10 760(4)	1 007(5)
N(11)	−315(4)	3 698(4)	4 803(4)	C(29)	−647(7)	10 656(5)	1 199(7)
N(12)	−795(4)	5 319(4)	3 471(3)	C(30)	306(4)	9 511(5)	1 555(5)
N(13)	−2 049(4)	7 403(4)	2 587(3)	C(31)	22(5)	8 518(5)	1 727(4)
C(1)	2 851(4)	5 694(5)	2 400(4)	C(32)	822(4)	7 192(4)	2 083(4)
C(2)	4 233(4)	5 375(5)	2 417(4)	C(33)	2 496(4)	1 871(4)	3 915(4)
C(3)	4 871(5)	6 100(4)	2 390(5)	C(34)	2 596(5)	1 156(5)	4 817(4)
C(4)	6 177(6)	5 528(6)	2 390(5)	C(35)	3 505(4)	34(5)	5 246(4)
C(5)	6 820(4)	4 269(6)	2 381(5)	C(36)	3 293(5)	−406(4)	6 121(4)
C(6)	6 162(5)	3 547(4)	2 384(5)	C(37)	2 199(6)	246(6)	6 512(3)
C(7)	4 852(4)	4 133(5)	2 434(4)	C(38)	1 292(4)	1 362(5)	6 071(4)
C(8)	3 857(4)	3 684(5)	2 444(4)	C(39)	1 525(5)	1 812(4)	5 220(4)
C(9)	3 246(4)	2 066(4)	2 468(4)	C(40)	809(5)	2 939(4)	4 576(4)
C(10)	3 655(4)	1 092(4)	1 951(4)	C(41)	−1 036(4)	4 750(4)	4 252(4)
C(11)	4 795(4)	72(5)	1 968(4)	C(42)	−2 303(5)	5 479(5)	4 539(4)
C(12)	4 902(4)	−687(4)	1 439(5)	C(43)	−2 964(6)	5 178(5)	5 246(4)
C(13)	3 895(6)	−432(5)	886(4)	C(44)	−4 200(6)	6 022(6)	5 297(5)
C(14)	2 752(4)	598(5)	863(4)	C(45)	−4 703(4)	7 136(6)	4 663(6)
C(15)	2 669(4)	1 340(4)	1 412(4)	C(46)	−4 012(5)	7 423(4)	3 957(4)
C(16)	1 625(4)	2 482(4)	1 532(4)	C(47)	−2 805(5)	6 559(4)	3 915(4)
C(17)	−348(4)	4 062(4)	1 055(4)	C(48)	−1 856(4)	6 499(4)	3 232(4)

Table 3 Selected bond lengths (Å) and angles (°)

In–N(1)	2.221(4)	In–N(3)	2.208(4)
In–N(5)	2.221(5)	In–N(7)	2.203(4)
In–N(10)	2.267(4)	In–N(12)	2.262(4)
Double N=C bonds			
N(2)–C(8)	1.276(8)	N(6)–C(24)	1.283(7)
N(7)–C(32)	1.303(7)	N(9)–C(33)	1.280(8)
N(13)–C(48)	1.271(7)		
Single N–C bonds			
N(2)–C(9)	1.441(8)	N(6)–C(25)	1.436(8)
N(3)–C(9)	1.493(5)	N(7)–C(25)	1.449(9)
N(9)–C(9)	1.443(7)	N(13)–C(25)	1.456(6)
Single C–C bonds			
C(9)–C(10)	1.523(9)	C(25)–C(26)	1.520(9)
N · · · N distances in trigonal prism			
N(1) · · · N(7)	2.846(12)	N(1) · · · N(3)	2.853(13)
N(1) · · · N(10)	3.320(16)	N(3) · · · N(5)	2.819(12)
N(3) · · · N(10)	2.793(12)	N(5) · · · N(7)	2.823(11)
N(5) · · · N(12)	3.343(15)	N(7) · · · N(12)	2.757(11)
N(10) · · · N(12)	2.881(12)		
N(1)–In–N(3)	80.2(2)	N(1)–In–N(5)	122.0(2)
N(3)–In–N(5)	79.1(2)	N(1)–In–N(7)	80.1(1)
N(3)–In–N(7)	136.5(2)	N(5)–In–N(7)	79.3(2)
N(1)–In–N(10)	95.4(2)	N(3)–In–N(10)	77.2(2)
N(5)–In–N(10)	130.8(2)	N(7)–In–N(10)	143.1(2)
N(1)–In–N(12)	129.5(2)	N(3)–In–N(12)	143.5(2)
N(5)–In–N(12)	96.4(2)	N(7)–In–N(12)	76.2(2)
N(10)–In–N(12)	79.0(1)		

isoindole units which is bridged by two additional isoindole rings. The resulting macrocyclic hexadentate chelate can also be described as two phthalocyaninate anions having one common half. The conjugation of the π-electron system in the inner 16-membered ring is interrupted at the two sp^3-hybridized bridgehead atoms C(9) and C(25) of the ring linkage to the bicyclic system and this is the reason for the two moieties not being planar. This is undoubtedly also the main reason for the specific green colour of the complex. The whole chelate ligand is an anion with three negative charges.

The hexadentate ligand is co-ordinated by six N atoms to the indium forming a distorted trigonal prism. Although the compound [Nb($C_{48}H_{24}N_{13}$)Cl] **2** contains a ligand of the same overall formula the ligand has a different structure and symmetry.[26] The main difference between the ligands is in the bridgehead atoms. In **1** the bridgehead C atoms belong to the two opposite isoindole rings of the phthalocyaninate moieties, whereas in **2** the bridgehead atoms belong to two neighbouring isoindole rings.

The C–N and C–C distances in the macrocyclic ligand fall into three and two groups, respectively. The six C–N bonds involving sp^3-hybridized bridgehead atoms, average 1.454 Å, are typical for single C–N bonds. Another five C–N bonds, average 1.282 Å, have a bond order of 2. The remaining fifteen C–N bonds, average 1.362 Å, are typical of conjugated π-electron systems and are comparable to those observed in other phthalocyanine structures.[27–30] The C(9)–C(10) and C(25)–C(26) bonds [1.523(9) and 1.520(9) Å] are typical single C–C bonds [1.530(15) Å].[31] Each of C(9) and C(25) forms four σ bonds, thus partially breaking the π-electron delocalization system. The remaining C–C bonds have intermediate distances between those of single and double bonds.

The dihedral angles between the two neighbouring mean least-squares planes of phthalocyaninate moieties are 105.9, 120.0 and 134.1°. For comparison the corresponding values are 114.0, 121.8 and 124.2° in complex **2**.[26] The differences may be explained by the different bridged phthalocyaninate moieties and additional co-ordination of Cl$^-$. The dihedral angles between the phenyl-ring planes from the same phthalocyanine moieties are 10.9, 18.1 and 24.7° for the C(34)–C(39) and

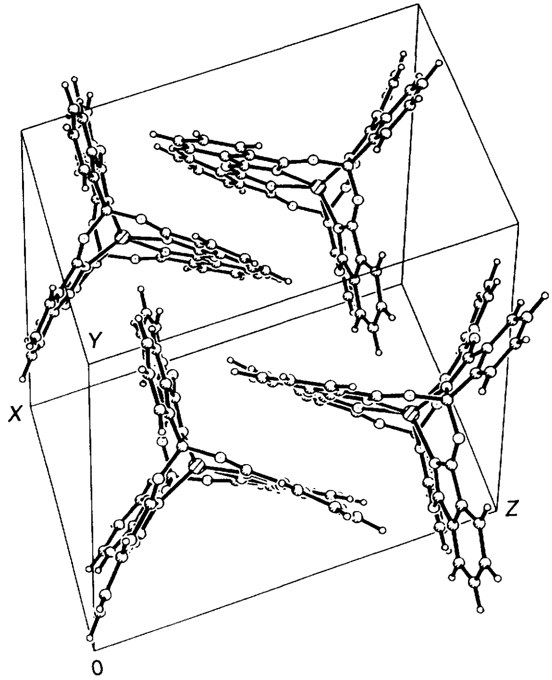


Fig. 2 The molecular arrangement in the unit cell of complex **1**

C(42)–C(47), C(10)–C(15) and C(18)–C(23) and C(2)–C(7) and C(25)–C(31) rings, respectively. The six phenyl rings are planar, the largest deviation from a plane being 0.026 Å for atom C(19) from the C(18)–C(23) ring. The means of the 36 C–C distances and C–C–C angles are 1.391 Å and 120.0°. Despite the normal C–C and C–C–C values, the phenyl rings are not perfectly hexagonal. Each of the six isoindole rings fused to the respective phenyl rings do not lie in the same plane. The values of the dihedral angles between the isoindole and fused phenyl ring planes are 1.2–7.6°.

The six In–N bond lengths range from 2.203(4) to 2.267(4) Å, comparable to those observed in an indium(III) porphyrin.[32] The displacements of the indium atom from the three planes defined by the four isoindole nitrogen atoms [N(1), N(3), N(5), N(7); N(1), N(7), N(10), N(12) and N(3), N(5), N(10), N(12)] are 0.947, 0.806 and 0.791 Å, respectively

The mutual arrangement of the molecules of complex **1** in the unit cell is shown in Fig. 2. The shortest intermolecular distance between two successive phthalocyaninate moieties is 3.25 Å (see Fig. 2), less than the van der Waals distance (3.4 Å) for aromatic carbon atoms,[33] and indicates weak interaction between the π-electron delocalization system from these planes. This interaction is also observed in the sandwich-type metallobisphthalocyanines.[34–39] The intermolecular contacts between nitrogen and hydrogen atoms are greater than 2.6 Å, the closest being 2.644 Å between N(4) and H(29) (x, $1+y$, z), 2.677 Å between N(2) and H(36) ($1-x$, $-y$, $1-z$) and 2.804 Å between N(13) and H(4) ($1+x$, y, z) showing that dimers are absent.

Conclusion

The characteristic feature of the crystal structure of complex **1** is the propeller-like shape of the molecules and their arrangement such that the wings from adjacent molecules interpenetrate to an extent similar to that in cog-wheels (see Fig. 2). This may be the explanation of the enhanced hardness of **1** in relation to [$In_2(pc)_3$] which possesses natural cleavage planes.[23]

The fact that the green **1** and violet [$In_2(pc)_3$] compounds possess similar compositions and coexist in the product of reaction of indium with 1,2-dicyanobenzene enables us to revise published data concerning lanthanide phthalocyaninates.[15–18,21,22,40,41] Kirin *et al.*[41] obtained a neodymium phthalocyaninate with the composition $Nd_2(pc)_3$, but assumed it to be $[Nd(pc)]^+[Nd(pc)_2]^-$. On the basis of our experimental data we are convinced that they also observed two kinds of phthalocyaninates isostructural with green **1** and violet [$In_2(pc)_3$].

Acknowledgements

We thank Professor Z. Gałdecki, Technical University of łódź, Poland, for the opportunity to use the SHELXTL program system in his laboratory. This research was supported by a grant (No. 2 P303 117 06) from the Polish State Committee for Scientific Research.

References

1 J. R. Ferraro and J. M. Williams, *Introduction to Synthetic Electrical Conductors*, Academic Press, Orlando, FL, 1987, p. 219.
2 A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 27.
3 M. Y. Opawa, J. Martinsen, S. M. Palmer, J. L. Stanton, J. Tanaka, R. L. Greene, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc.*, 1987, **109**, 1115.
4 T. Inabe, J. G. Gaudiello, M. K. Moguel, J. W. Lyding, R. L. Pruston, W. J. McCarthy, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, 1986, **108**, 7595.
5 F. H. Moser and A. L. Thomas, *Phthalocyanine Compounds*, Van Nostrand-Reinhold, Princeton, NJ, 1963.
6 M. Almeida, M. G. Kanatsidis, L. M. Tonge, T. J. Marks, H. O. Marcy, W. J. McCarthy and C. R. Kannewurf, *Solid State Commun.*, 1987, **63**, 457.
7 K. J. Wynne, *Inorg. Chem.*, 1984, **23**, 4658.
8 W. J. Kroenke, L. E. Sutton, R. D. Joyner and M. E. Kenny, *Inorg. Chem.*, 1962, **2**, 1064.
9 J. P. Linsky, T. R. Paul, R. S. Nohr and M. E. Kenny, *Inorg. Chem.*, 1980, **19**, 3131.
10 K. J. Wynne, *Inorg. Chem.*, 1985, **24**, 2040.
11 P. M. Kuznesof, K. J. Wynne, R. S. Nohr and M. E. Kenny, *J. Chem. Soc., Chem. Commun.*, 1980, 121.
12 R. S. Hohr, P. M. Kuznesof, K. J. Wynne, M. E. Kenny and P. G. Siebenman, *J. Am. Chem. Soc.*, 1981, **103**, 4371.
13 P. Brant, R. S. Nohr, K. J. Wynne and D. Weber, *Mol. Cryst. Liq. Cryst.*, 1982, **81**, 255.
14 R. S. Nohr and K. N. Wynne, *J. Chem. Soc., Chem. Commun.*, 1981, 1210.
15 I. S. Kirin, P. N. Moskalev and Yu A. Makashev, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1965, **10**, 1065.
16 I. S. Kirin, P. N. Moskalev and Yu A. Makashev, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1967, **12**, 369.
17 S. Misumi and K. Kasuga, *Nippon Kagaku Zasshi*, 1971, **92**, 335.
18 A. G. McKay, J. F. Boas and G. J. Troup, *Aust. J. Chem.*, 1974, **27**, 955.
19 G. A. Corker, B. Grant and N. J. Clecak, *J. Electrochem. Soc.*, 1979, **126**, 1339.
20 M. Moussavi, A. De Cian, J. Fischer and R. Weiss, *Inorg. Chem.*, 1988, **27**, 1287.
21 I. S. Kirin and P. N. Moskalev, *Russ. J. Phys. Chem.*, 1967, **41**, 251.
22 M. Yamana, *Res. Rep. Tokyo Denki Univ.*, 1977, **25**, 39.
23 J. Janczak and R. Kubiak, *J. Chem. Soc., Dalton Trans.*, 1993, 3809.
24 R. Kubiak and J. Janczak, *J. Alloys Comp.*, 1993, **200**, L7.
25 G. M. Sheldrick, SHELXTL PC program system, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
26 F. Gingl and J. Stahle, *Acta Crystallogr., Sect. C*, 1990, **46**, 1841.
27 R. Kubiak and J. Janczak, *J. Alloys Comp.*, 1992, **189**, 107.
28 J. Janczak and R. Kubiak, *J. Alloys Comp.*, 1992, **190**, 121.
29 R. Kubiak and J. Janczak, *J. Alloys Comp.*, 1992, **190**, 117.
30 J. Janczak and R. Kubiak, *J. Alloys Comp.*, 1993, **202**, 69.
31 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
32 R. G. Ball, K. M. Lee, A. G. Marshall and J. Trotter, *Inorg. Chem.*, 1980, **19**, 1463.
33 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 1962, p. 262.
34 A. Gieren and W. Hoppe, *Chem. Commun.*, 1971, 413.
35 W. E. Bennet, D. E. Broberg and N. C. Baenziger, *Inorg. Chem.*, 1973, **12**, 930.

36 J. Janczak and R. Kubiak, *J. Alloys Comp.*, 1994, **204**, 5.
37 I. S. Kirin, A. B. Kolabin and A. A. Lyczev, *Zh. Struct. Khim.*, 1974, **15**, 486.
38 A. N. Darovskikh, O. V. Frank-Kamenestskaya, V. S. Fukholamenskij and P. N. Moskalev, *Kristallografiya*, 1984, **29**, 455.
39 K. Kasuga and M. Tsutsui, *Coord. Chem. Rev.*, 1980, **32**, 67.
40 C. Clarisse and M. T. Riou, *Inorg. Chim. Acta*, 1987, **130**, 139.
41 I. S. Kirin, P. N. Moskalev and N. W. Iwannikova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1967, **12**, 497.

Received 15*th February* 1994; *Paper* 4/00918E