Hg_3^{2+} cation but this peak rapidly diminishes and is replaced by peaks at 248 and 280 nm. The peak at 248 nm is due to the Hg_2^{2+} ion while the peak at 280 nm is due to the SO_2 formed as the reduction product of HSO_3F.

Registry No. Hg, 7439-97-6; SbF_5, 7783-70-2; AsF_5, 7784-36-3; HSO_3F, 7789-21-1; $Hg_2(AsF_6)_2$, 38832-78-9; $Hg_3(Sb_2F_{11})_2$, 38832-79-0; $Hg_3(AsF_6)_2$, 34738-00-6; $Hg_3(SO_3F)_2$, 38768-48-8.

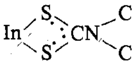
Contribution from the Department of Chemistry,
North Carolina State University, Raleigh, North Carolina 27607

Preparation and Crystal and Molecular Structure of Tris(pentamethylenedithiocarbamato)indium(III), In(pmtc)$_3$

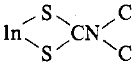
P. J. HAUSER, J. BORDNER, and A. F. SCHREINER*

Received August 3, 1972

The three-dimensional X-ray crystal structure determination of tris(pentamethylenedithiocarbamato)indium(III), In(pmtc)$_3$ or $In(S_2CNC_5H_{10})_3$, was carried out, and relationships of these crystallographic data to other electronic structural features of the $M^{III}S_6$ chromophore are pointed out. The following conclusions are reached: (1) the pair of carbon-sulfur p_π electrons of carbamate in



are delocalized; (2) the nitrogen atom π bonds significantly with carbon of (S_2CN), since this C-N distance is significantly (0.15 Å) shorter than the N-C distance involving the six-membered organic ring carbon atoms; (3) the last mentioned C-N distance of 1.33 Å is also 0.07 Å shorter than the sum of radii of an sp^2 carbon and a saturated amine nitrogen; (4) the seven-atom group



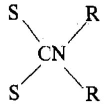
is planar; (5) the three organic rings have the chair conformation; (6) the S-In-S chelate angle is only 69°; (7) the chelate projection angle, ϕ, or (propeller) pitch angle, is only 25°, bringing the structure *closer to a trigonal prism* ($\phi = 0°$) *than an octahedron* ($\phi = 60°$); (8) trigonal crystal field Hamiltonians should be allowed to depend on two independent angles, the polar angle θ and chelate projection angle ϕ, so as to retain general applicability.

Introduction

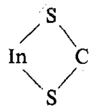
Compounds containing metal-sulfur bonds have occupied a position of special interest from several points of view, *e.g.*, their biochemistry,[1] inorganic chemistry,[2] synthetic chemistry,[2,3] spectroscopy,[2-8] and theoretical features.[3,8] The early works of Kida and Yoneda[9] and Jorgensen[2,10] are especially noteworthy, and the latter author is largely responsible for stimulating a number of more recent detailed investigations.[2-5,8] Some of these more interesting recent questions have dealt with both static structural details and electronic structure problems of electronic ground and excited states. This study will be concerned primarily with the complexed ligand pentamethylenedithiocarbamate, pmtc$^-$, as found in the tris-bidentate chelate complex In(pmtc)$_3$. This complex and the chromium(III) analog, Cr(pmtc)$_3$ (Figure 1), were first prepared by Schreiner and Hauser.[3] Partly due to the interesting nature of the magnetic circular dichroism spectra of M(tc)$_3$[3,8] and because of the interest in the structural details of intraligand chelate angle ζ (Figure 2), chelate projection angle ϕ (Figure 3), and trigonal polar angle θ (Figures 2 and 3), the present study of In(pmtc)$_3$ was undertaken. The relationship of these parameters, their relationship to formulating six-coordinate trigonal crystal field Hamiltonians, and several other electronic structural problems will be discussed.

Discussion

From Figure 4, which shows several averaged interatomic distances and bond angles, it is immediately interesting to point to several features. First, the In-S bond distances in any one [In(pmtc)] moiety are equal (2.59 Å), and this holds for each of the three moieties. This result is entirely consistent with the view that the pair of S-C π electrons of



are completely delocalized in the four-member ring



when the ligand coordinates to the metal. This result is in

---

(1) S. Livingstone and A. E. Mihkelson, *Inorg. Chem.*, **9**, 2545 (1970).
(2) C. K. Jorgensen, *Inorg. Chim. Acta Rev.*, **2**, 65 (1968).
(3) P. J. Hauser, A. F. Schreiner, J. D. Gunter, W. J. Mitchell, and M. K. DeArmond, *Theor. Chim. Acta*, **24**, 78 (1972).
(4) J. D. Lebedda and R. A. Palmer, *Inorg. Chem.*, **10**, 2704 (1971).
(5) J. D. Lebedda and R. A. Palmer, *Inorg. Chem.*, **11**, 484 (1972).
(6) A. A. G. Tomlinson, *J. Chem. Soc. A*, 1409 (1971).
(7) J. R. Wasson, S. J. Wasson, and G. M. Woltermann, *Inorg. Chem.*, **9**, 1576 (1970).
(8) A. F. Schreiner and P. J. Hauser, *Inorg. Chem.*, **11**, 2706 (1972).
(9) S. Kida and H. Yoneda, *J. Chem. Soc. Jap.*, **76**, 1059 (1955).
(10) C. K. Jorgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

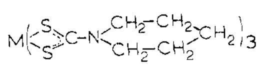


Figure 1. Tris(pentamethylenedithiocarbamato)metalate(III).

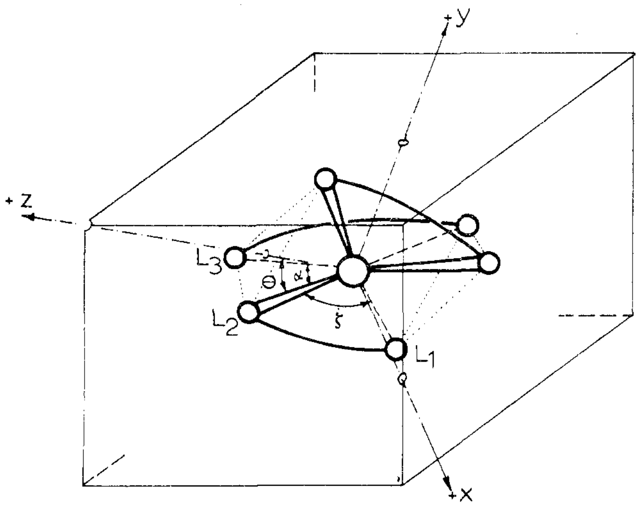


Figure 2. The relationships among several angles in a tris(bidentate)-metalate moiety: ζ is the chelate angle, θ is the angle between the M-L vector and the molecular C_3 axis ($\equiv z$ axis), and α relates one metal-ligand vector, M-L_A, to another, M-L_B.

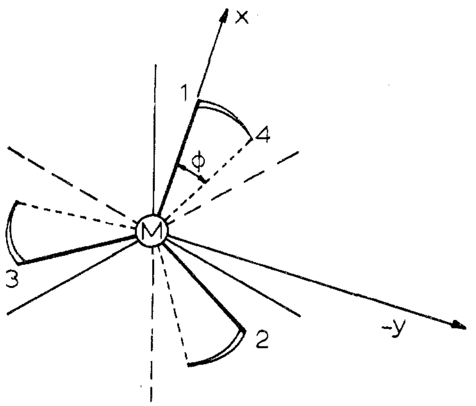


Figure 3. The projection of chelate angle ζ, onto the x,y plane (plane of the paper) generating angle ϕ, the *chelate projection angle.* In practice ϕ varies from 60° (octahedron) to 25°, and in principle its limit could be 0° (trigonal prism). One might also refer to ϕ as the (propeller) *pitch angle.*

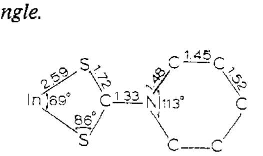
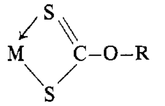


Figure 4. Averaged bond distances and angles in In(pmtc)$_3$.

sharp contrast to the similar complexes of Sb(III) and As(III), *i.e.*, tris(ethyl xanthato)antimony(III) and the arsenic analog,[11] where the metal-sulfur distances are distinctly nonequivalent, thus giving rise to nondelocalized structures. However, equal S-C bonds such as in In(pmtc)$_3$ were also observed in the following complex carbamate molecules: tris(diethyldithiocarbamato)indium(III), In(detc)$_3$,[12] Co(detc)$_3$,[13] and Fe(n-Butc)$_3$.[14] Very interestingly we see that only the $(n + 1)s^2$ lone-pair ions (As^{3+}, Sb^{3+}) contain significantly nonequivalent sulfur-carbon bonds.



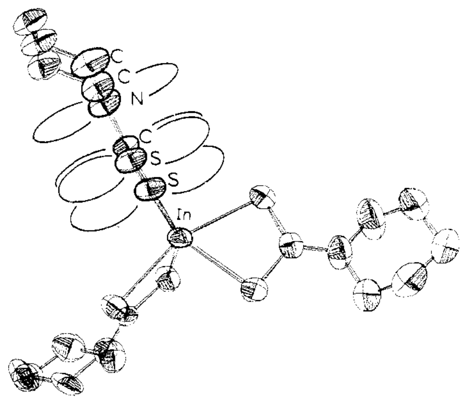
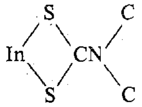
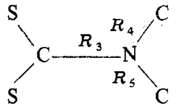


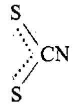
Figure 5. Projection of In(pmtc)$_3$ which demonstrates the near planarity of



The second interesting feature from Figure 4 is that the R_3(C-N) bond length of 1.33 Å is shorter than R_4(C-N) (1.45-1.52 Å) of the fragment

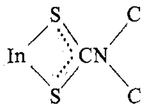


Even if one takes into account that the sp^2 carbon atom ought to have the smaller radius (0.74 Å), it is reasonable to conclude some C-N multiple bonding. The experimental distance of 1.33 Å is 0.07 Å shorter than the sum of these C(sp^2) and N radii. This leads us to conclude that the nitrogen atom is very involved in π bonding to the carbon of



or equivalently to the π system of the three atoms

The results of semiempirical LCAO-MO calculations on the simpler Cr(H$_2$tc)$_3$ pointed to the same conclusion.[8] The immediate expected consequence of this conclusion is that the seven-atom moiety



should then be planar. Indeed this is what was observed as is demonstrated in Figure 5, where we have drawn p$_\pi$ orbitals to emphasize the point. A similar observation was made for Co(detc)$_3$ by Merlino.[13] The occurrence of this planarity

---

[11] (a) G. Carrsi and G. Gottardi, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 113, 373 (1960); (b) G. Gottardi, *ibid.*, 115, 451 (1961).

[12] Personal communication from G. J. Palenik to A. A. G. Tomlinson.

[13] S. Merlino, *Acta Crystallogr., Sect. B*, 24, 1441 (1968).

[14] B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 1517 (1968).

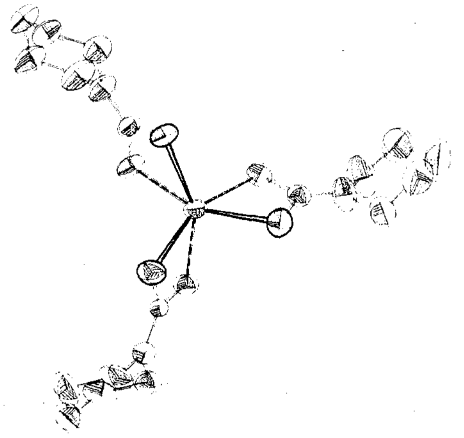
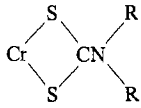


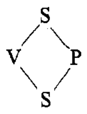
Figure 6. Trigonal view of In(pmtc)$_3$ (with C_3 axis only approximately perpendicular to plane of paper).

appears well suited to carry out studies of substituent effects as R_3 is varied in

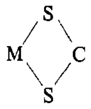


since σ effects should be separable from π effects.

We now make reference to the trigonal view (along the "C_3" molecular axis) as shown in Figure 6. If the sulfur atoms of InS_6 were placed at corners of a perfect octahedron, projection angle ϕ (Figures 2 and 3) would be 60°. It is clear that this projection angle of the chelate angle ζ (Figure 2) is significantly less than 60°; indeed it is *ca.* 25°! It is most interesting to compare this projection angle ϕ for a number of structures containing the MS_6 coordination sphere. The values of ϕ are as follows: V(detp)$_3$, ~60°;[15] Co(detc)$_3$, ~44°;[13] Fe(exan)^3, ~41°;[16] Fe(n-Butc)$_3$, ~34°;[14] In(pmtc)$_3$, ~25° (this work). Thus in In(pmtc)$_3$ the structure is beginning to approach a trigonal prism on the basis of the MS_6 group of atoms. At least the geometry of MS_6 ($\phi = 25°$) is more than halfway between the perfect octahedron ($\phi = 60°$) and the trigonal prism ($\phi = 0°$)! The pitch angle ϕ of V(detp)$_3$ has the *octahedral* value presumably due to the greater size of P in

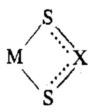


compared to C in



which can have the effect of increasing ζ and subsequently ϕ.

The chelate angle ζ is also quite variable in the four-membered rings



Thus, in In(pmtc)$_3$ $\zeta = 69.3°$, whereas values of ζ range from 69.6 to 81.4° for V(detp)$_3$,[15] In(detc)$_3$,[12] In(detp)$_3$,[17] and Co(detc)$_3$.[13] However, the angles are very similar for In(detc)$_3$ (69.6°) and In(pmtc)$_3$ (69.3°), but it is somewhat large for Co(detc)$_3$ (76.5°).

Table I. Crystal and Data Collection Parameters

Molecular formula	$In(S_2CNC_5H_{10})_3$
Mol wt	595.7
Crystal size (data collection)	0.15 × 0.20 × 0.20 mm
Cell dimensions	$a = 11.747$ (7) Å
	$b = 18.77$ (1) Å
	$c = 11.561$ (7) Å
	$\beta = 91.60$ (5)°
	$V = 2548$ (3) Å^3
Space group	$P2_1/n$
Molecules/unit cell	4
Density calcd ($Z = 4$)	1.55 g/cm^3
Density obsd	1.52 g/cm^3
Scan technique	θ-2θ
Scan width	1.2° below Kα_1, 1.2° above Kα_2
Scan speed	2°/min in 2θ
Background count time	One-half scan time on each side of peak
No. of reflections	2750
Nonzero reflections[a]	2609

[a] All intensities with values less than or equal to zero were set equal to zero with zero weight.

Table II. Final Positional Parameters and Their Standard Deviations

Atom no.	Atom type	x	y	z
1	In	0.25877 (6)	0.36397 (3)	0.20305 (6)
2	S	0.44853 (22)	0.31228 (14)	0.28575 (22)
3	S	0.42938 (22)	0.41153 (15)	0.08890 (22)
4	C	0.51382 (79)	0.36389 (50)	0.18573 (78)
5	N	0.62582 (69)	0.36949 (52)	0.18113 (70)
6	C	0.68649 (95)	0.41282 (68)	0.09623 (106)
7	C	0.76992 (130)	0.37312 (79)	0.04139 (150)
8	C	0.85642 (120)	0.33963 (93)	0.12934 (193)
9	C	0.79095 (113)	0.29809 (80)	0.21791 (147)
10	C	0.70315 (109)	0.33532 (89)	0.26740 (113)
11	S	0.18412 (22)	0.26463 (13)	0.06636 (21)
12	S	0.13824 (23)	0.27305 (14)	0.31597 (21)
13	C	0.12559 (76)	0.22751 (48)	0.18593 (84)
14	N	0.07471 (70)	0.16497 (45)	0.18062 (64)
15	C	0.05984 (89)	0.12273 (55)	0.07267 (82)
16	C	−0.05465 (89)	0.09405 (56)	0.05738 (85)
17	C	−0.09038 (92)	0.05053 (57)	0.15980 (89)
18	C	−0.07679 (101)	0.09575 (62)	0.26932 (91)
19	C	0.03753 (104)	0.12496 (62)	0.28423 (86)
20	S	0.23754 (22)	0.46547 (14)	0.35261 (24)
21	S	0.11727 (23)	0.45934 (15)	0.12617 (24)
22	C	0.14630 (72)	0.50413 (47)	0.25376 (89)
23	N	0.09727 (66)	0.56721 (43)	0.27442 (83)
24	C	0.01253 (102)	0.60069 (60)	0.19644 (111)
25	C	−0.09911 (97)	0.60524 (74)	0.25646 (127)
26	C	−0.08847 (105)	0.64159 (67)	0.37120 (132)
27	C	0.00497 (113)	0.60918 (64)	0.44610 (112)
28	C	0.11396 (96)	0.60540 (61)	0.38329 (115)

Interesting too is the chair conformation of the six-membered pentamethylene-nitrogen ring (Figures 5, 6). This conformation is present in each of the three rings. Furthermore, the planes of these rings are approximately codirectional, and intramolecularly one ring can be rotated approximately into the other *via* the molecular "C_3" axis (Figure 6).

The structural parameters and conclusions discussed above have several other important consequences in areas of electronic structure elucidation and theory. In this respect, a new trigonal crystal field Hamiltonian was recently proposed[18] for ML_6 in which angle θ, but not ϕ, was allowed to exist as a variable parameter. This immediately limits the use of the

---

(15) C. Furlani, A. A. G. Tomlinson, P. Porta, and A. Sgamellotti, *J. Chem. Soc. A*, 2929 (1970).

(16) B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 45 (1970).

(17) P. Coggon, J. D. Lebedda, A. T. McPhail, and R. A. Palmer, *Chem. Commun.*, 78 (1970).

(18) A. B. P. Lever and B. R. Hollebone, *J. Amer. Chem. Soc.*, 94, 1816 (1972).

Table III. Thermal Vibrational Parameters and Their Standard Deviations

Atom no.	Atom type	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
1	In	0.00683 (6)	0.00169 (2)	0.00785 (7)	0.00005 (6)	−0.00163 (9)	−0.00033 (6)
2	S	0.00809 (24)	0.00277 (9)	0.00768 (24)	0.00193 (25)	−0.00098 (40)	0.00112 (25)
3	S	0.00776 (24)	0.00325 (10)	0.00821 (25)	0.00028 (26)	−0.00081 (40)	0.00300 (27)
4	C	0.00667 (90)	0.00264 (33)	0.00695 (86)	0.00076 (95)	−0.00011 (141)	−0.00223 (96)
5	N	0.00673 (80)	0.00587 (44)	0.00822 (83)	0.00164 (99)	−0.00001 (136)	0.00233 (104)
6	C	0.00880 (116)	0.00472 (52)	0.01469 (141)	0.00168 (131)	0.00492 (213)	0.00171 (150)
7	C	0.01342 (159)	0.00565 (69)	0.02405 (215)	−0.00234 (172)	0.01000 (315)	0.00380 (207)
8	C	0.00939 (147)	0.00703 (82)	0.04626 (371)	0.00100 (175)	0.01458 (393)	0.01476 (290)
9	C	0.00942 (137)	0.00508 (60)	0.03020 (241)	0.00264 (151)	−0.00362 (297)	0.00632 (206)
10	C	0.00955 (125)	0.00917 (84)	0.01351 (144)	0.00658 (173)	−0.00024 (230)	0.00635 (185)
11	S	0.00961 (26)	0.00217 (8)	0.00650 (22)	−0.00197 (24)	−0.00090 (39)	−0.00018 (23)
12	S	0.01066 (28)	0.00256 (9)	0.00670 (23)	−0.00302 (26)	−0.00010 (41)	−0.00133 (25)
13	C	0.00632 (85)	0.00190 (32)	0.00962 (100)	−0.00161 (88)	−0.00139 (149)	0.00014 (96)
14	N	0.01026 (86)	0.00335 (32)	0.00567 (73)	−0.00408 (88)	−0.00288 (129)	−0.00039 (83)
15	C	0.00985 (107)	0.00349 (43)	0.00709 (94)	−0.00164 (109)	−0.00041 (163)	−0.00092 (106)
16	C	0.01041 (111)	0.00315 (39)	0.00849 (101)	−0.00303 (112)	−0.00319 (170)	−0.00150 (111)
17	C	0.01094 (111)	0.00310 (39)	0.00902 (102)	−0.00496 (113)	−0.00169 (174)	0.00077 (111)
18	C	0.01390 (133)	0.00348 (43)	0.00902 (108)	−0.00572 (129)	0.00277 (196)	0.00087 (119)
19	C	0.01504 (140)	0.00436 (50)	0.00697 (98)	−0.00636 (137)	−0.00371 (191)	0.00108 (118)
20	S	0.00731 (24)	0.00240 (9)	0.01045 (27)	0.00112 (24)	−0.00396 (42)	−0.00288 (26)
21	S	0.00885 (26)	0.00270 (9)	0.01014 (28)	0.00221 (26)	−0.00398 (44)	0.00062 (28)
22	C	0.00471 (77)	0.00142 (30)	0.01330 (117)	−0.00006 (81)	0.00353 (154)	0.00016 (99)
23	N	0.00648 (76)	0.00225 (31)	0.01690 (116)	0.00045 (82)	0.00230 (154)	0.00126 (101)
24	C	0.01208 (127)	0.00279 (40)	0.01727 (149)	0.00659 (127)	0.00202 (230)	0.00473 (140)
25	C	0.00769 (111)	0.00534 (57)	0.02059 (176)	0.00617 (135)	0.00201 (237)	0.00650 (179)
26	C	0.01066 (129)	0.00392 (50)	0.02207 (187)	0.00364 (136)	0.01228 (268)	0.00282 (167)
27	C	0.01415 (141)	0.00319 (43)	0.01650 (155)	0.00419 (135)	0.00239 (254)	−0.00214 (141)
28	C	0.00870 (113)	0.00301 (41)	0.01996 (163)	0.00155 (115)	−0.00349 (224)	−0.00692 (147)

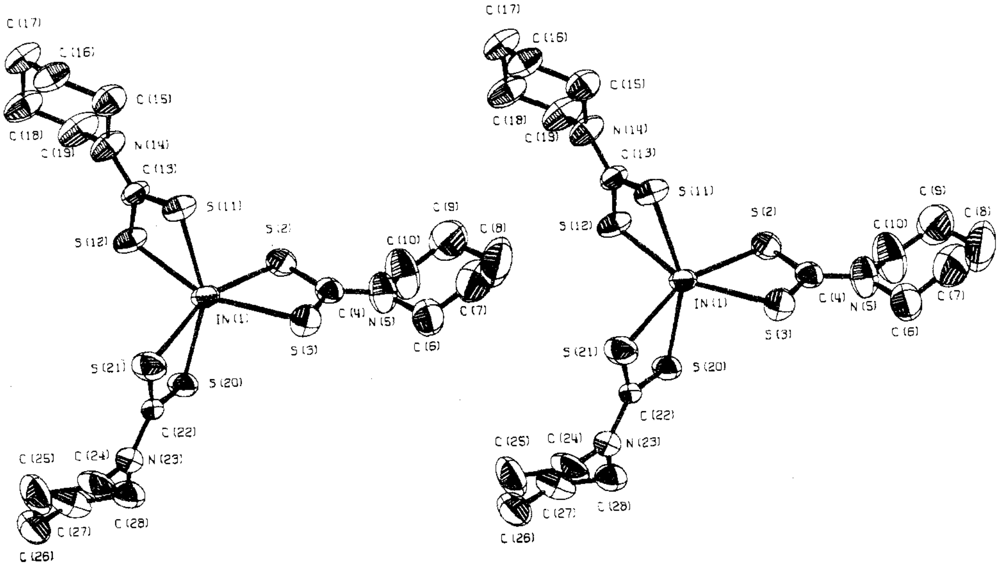


Figure 7. Atom labels for Tables I–IV. This is also a stereodrawing of In(pmtc)$_3$.

Hamiltonian, since the correct form in the coordinate system of Figure 3 is

$$V_{\text{trig}} = eq\left(\frac{r^2}{R^3}\right)6\sqrt{\frac{\pi}{5}}(3\cos^2\theta - 1)Y_2{}^0 + eq\left(\frac{r^4}{R^5}\right)\times \frac{3\sqrt{\pi}}{2}\left(\frac{35}{3}\cos^4\theta - 10\cos^2\theta + 1\right)Y_4{}^0 + eq\left(\frac{r^4}{R^5}\right)\sqrt{35\pi}\left[\sin^3\theta\cos\theta\sin\left(\frac{3}{2}\phi\right)\right]Y_4{}^{-3} - Y_4{}^3$$

In other words, polar angle θ as well as projection angle ϕ occur in V_{trig}, and from the early part of the discussion the variation of ϕ is large enough so as to retain it as a variable. It is in this respect that trigonal crystal field calculations which employ v and v' as variables are quite satisfactory, since

$$v = -3\left[-\frac{3}{7}(3\cos^2\theta - 1)\right]\langle R_2\rangle - \frac{5}{21}\left(\frac{35}{3}\cos^4\theta - 10\cos^2\theta + 1\right)\langle R_4\rangle - \frac{5\sqrt{2}}{9}\left[\sin^3\theta\cos\theta \times \sin\left(\frac{3}{2}\phi\right)\right]\langle R_4\rangle$$

and

$$v' = \frac{3\sqrt{2}}{7}(3\cos^2\theta - 1)\langle R_2\rangle - \frac{5\sqrt{2}}{28}\left(\frac{35}{3}\cos^4\theta - 10\cos^2\theta + 1\right)\langle R_4\rangle - \frac{5}{6}\left[\sin^3\theta\cos\theta\sin\left(\frac{3}{2}\phi\right)\right]\langle R_4\rangle$$

where

$$R_k = \left\langle R_n{}^k \left[\frac{r<^k}{r>^{k+1}} \right] R_n{}^k \right\rangle$$

Finally, it is worth investigating how the "bite" (intraligand S-S distance) and "compression ratio s/h" as recently defined[19,20] compare with those of other MS_6 chelates. s would be defined here as the interligand S-S distance between any pair of such atoms having $+z$ coordinates (*e.g.*, coordinated atoms L_2 and L_3) or between any pair with $-z$ coordinates (refer to Figure 2). Distance h was defined as the separation of two planes, one containing the three sulfur atoms on the $+z$ side of the molecule and the other one containing the three sulfur atoms on the $-z$ side (Figure 2). The compression ratio for $In(pmtc)_3$, s/h, is 1.41 whereas for an octahedron the value would be 1.22.[20] Thus, the three chelate fragments

are not only twisted ($\phi = 25°$) compared to the octahedron ($\phi = 60°$) but also more compressed "into the metal" (our $s/h = 1.41$ compared to the octahedral value of $s/h = 1.22$).

In another D_3 carbamato complex, $[Ni(Butc)_3]^+$ the value of s/h is only 1.36.[20] Small differences of compression ratios such as just mentioned may not be significant, however, since the bites of the two carbamates are not the same (b = 2.95 Å in $In(pmtc)_3$ and b = 2.79 Å in $[Ni(Butc)_3]^+$). On the other hand, $In(pmtc)_3$ is the most "compressed" MS_6 chelate reported to date.[20]

Table IV. Bond Lengths in $In(pmtc)_3$

Atom no.	Atom types	Distance, Å	Atom no.	Atom types	Distance, Å
1-2	In-S	2.590 (3)	5-6	N-C	1.474 (15)
1-3	In-S	2.589 (3)	5-10	N-C	1.477 (16)
1-11	In-S	2.582 (3)	14-15	N-C	1.485 (12)
1-12	In-S	2.593 (3)	14-19	N-C	1.490 (13)
1-20	In-S	2.589 (3)	23-24	N-C	1.466 (15)
1-21	In-S	2.584 (3)	23-28	N-C	1.457 (16)
2-4	S-C	1.707 (10)	6-7	C-C	1.397 (20)
3-4	S-C	1.726 (10)	7-8	C-C	1.551 (25)
11-13	S-C	1.709 (10)	8-9	C-C	1.514 (25)
12-13	S-C	1.732 (10)	9-10	C-C	1.383 (20)
20-22	S-C	1.707 (10)	15-16	C-C	1.455 (15)
21-22	S-C	1.724 (10)	16-17	C-C	1.508 (15)
4-5	C-N	1.323 (12)	17-18	C-C	1.529 (15)
13-14	C-N	1.318 (12)	18-19	C-C	1.457 (17)
22-23	C-N	1.341 (12)	24-25	C-C	1.503 (17)
			25-26	C-C	1.500 (18)
			26-27	C-C	1.507 (19)
			27-28	C-C	1.491 (18)

Experimental Section

Compound Preparation and Crystal Growth. Tris(pentamethylenedithiocarbamato)indium(III), $In(pmtc)_3$, was prepared by mixing freshly prepared aqueous solutions of $Na(pmtc)\cdot 2H_2O$ (made by the method of Gleu and Schwab[21]) and anhydrous $InCl_3$ (obtained from Alfa Inorganics) in a 3:1 ligand:metal mole ratio. The white precipitate of $In(pmtc)_3$ formed immediately and was removed by suction filtration. After air drying, the white powder was dissolved in acetone and the solution allowed to evaporate slowly. Colorless rectangular plates suitable for X-ray analysis were obtained.

X-Ray Analysis of $In(pmtc)_3$. A platelike crystal of $In(pmtc)_3$ was cut to a suitable size (0.60 mm × 0.15 mm × 0.10 mm) and surveyed for crystal quality on a precession camera. Approximate unit cell dimensions and space group were obtained from this survey. Final unit cell dimensions were obtained at room temperature on a Syntex $P\bar{1}$, four-circle diffractometer using a least-squares fit of six high-angle reflections ($2\theta > 21°$) using molybdenum radiation (λ 0.71069 Å). Systematic absences indicated space group $P2_1/n$ ($h0l$, $h + 1 = 2n + 1$; $0k0$, $k = 2n + 1$). The density of the crystal was measured by the flotation technique in aqueous potassium iodide.

A smaller crystal (0.15 mm × 0.20 mm × 0.20 mm) was mounted in a general orientation for data collection. An intensity data set to a resolution of 1 Å (maximum ($\sin\theta)/\lambda = 0.5$) was collected on the Syntex $P\bar{1}$ diffractometer equipped with a graphite monochromator. The incident beam monochromator was mounted in the perpendicular mode. Polarization effects due to the monochromator were corrected for by a method suggested by Azaroff.[22] The radiation detecting system consisted of a scintillation counter (NaI(Tl) crystal) and pulse height analyzer. A single check reflection was monitored every 30 reflections and revealed no radiation damage since its variation was

Table V. Bond Angles in $In(pmtc)_3$

Atom no.	Atom types	Angle, deg
2-1-3	S-In-S	69.3 (0.1)
11-1-12	S-In-S	69.6 (0.1)
20-1-21	S-In-S	69.3 (0.1)
3-1-11	S-In-S	101.1 (0.1)
3-1-21	S-In-S	94.9 (0.1)
11-1-21	S-In-S	94.9 (0.1)
2-1-12	S-In-S	92.5 (0.1)
2-1-20	S-In-S	97.3 (0.1)
12-1-20	S-In-S	94.8 (0.1)
2-1-11	S-In-S	103.3 (0.1)
2-1-21	S-In-S	157.8 (0.1)
3-1-12	S-In-S	157.6 (0.1)
3-1-20	S-In-S	100.2 (0.1)
11-1-20	S-In-S	154.5 (0.1)
12-1-21	S-In-S	105.9 (0.1)
1-2-4	In-S-C	86.3 (0.3)
1-3-4	In-S-C	86.0 (0.3)
1-11-13	In-S-C	86.4 (0.3)
1-12-13	In-S-C	85.6 (0.3)
1-20-22	In-S-C	86.3 (0.3)
1-21-22	In-S-C	86.2 (0.3)
2-4-3	S-C-S	118.2 (0.5)
11-13-12	S-C-S	118.3 (0.5)
20-22-21	S-C-S	118.1 (0.5)
2-4-5	S-C-N	122.6 (0.7)
3-4-5	S-C-N	119.2 (0.7)
11-13-14	S-C-N	121.2 (0.7)
12-13-14	S-C-N	120.5 (0.7)
20-22-23	S-C-N	121.4 (0.8)
21-22-23	S-C-N	120.5 (0.7)
4-5-6	C-N-C	124.8 (0.9)
4-5-10	C-N-C	122.2 (0.9)
13-14-15	C-N-C	123.9 (0.8)
13-14-19	C-N-C	123.7 (0.8)
22-23-24	C-N-C	123.8 (0.9)
22-23-28	C-N-C	122.7 (0.9)
6-5-10	C-N-C	112.9 (0.9)
15-14-19	C-N-C	112.1 (0.8)
24-23-28	C-N-C	113.1 (0.8)
5-6-7	N-C-C	111.5 (1.1)
5-10-9	N-C-C	113.1 (1.2)
14-15-16	N-C-C	112.7 (0.8)
14-19-18	N-C-C	112.6 (0.9)
23-24-25	N-C-C	109.1 (1.0)
23-28-27	N-C-C	110.3 (0.9)
6-7-8	C-C-C	112.0 (1.4)
7-8-9	C-C-C	108.4 (1.2)
8-9-10	C-C-C	114.7 (1.3)
15-16-17	C-C-C	112.4 (0.9)
16-17-18	C-C-C	108.9 (0.9)
17-18-19	C-C-C	112.4 (0.9)
24-25-26	C-C-C	112.5 (1.0)
25-26-27	C-C-C	111.5 (1.1)
26-27-28	C-C-C	111.2 (1.1)

---

(19) D. L. Kepert, *Inorg. Chem.*, 11, 1562 (1972).

(20) E. I. Stiefel and G. F. Brown, *Inorg. Chem.*, 11, 434 (1972).

(21) K. Gleu and R. Schwab, *Angew. Chem.*, 62, 320 (1950).

(22) L. V. Azaroff, *Acta Crystallogr.*, 8, 701 (1955).

well within counter statistics. Details of the crystal and data collection parameters are summarized in Table I.

The diffractometer output was processed and all subsequent crystallographic computations were made using subprograms of the CRYM crystallographic computer system.[23] The processing included corrections for background, Lorentz, and polarization effects. Polarization due to the monochromator was included in these corrections. Processing also included the calculation of F^2 and its standard deviation for each reflection. The standard deviations were assigned on the basis of the following equation: $\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2$, where S is the number of counts collected during the scan, B_1 and B_2 are the background counts, d is an empirical constant set at 0.02, and α is the scan time to total background time ratio.

Finally, the data were placed on an absolute scale by Wilson[24] statistics. Atomic scattering factors were taken from the following sources: C, S, N, "International Tables for X-Ray Crystallography";[25] H, Stewart, Davidson, and Simpson;[26] In, Cromer and Mann.[27] The scattering factor for In was corrected for the real anomalous scattering component, $\Delta f'$.[28] While no corrections were made for absorption, this effect was minimized by using a smaller crystal during data collection (see Table I). The absorption coefficient, μ, was 14.0 cm^{-1}. The maximum and minimum transmission factors were 76 and 63% which correspond to a maximum error in F of about 5%.

Determination of Structure and Refinement. A trial structure was obtained by conventional Patterson and Fourier techniques. The equivalent positions used for space group $P2_1/n$ were $\pm(x, y, z)$ and $\pm(^1/_2 + x, ^1/_2 - y, ^1/_2 + z)$. This trial structure refined smoothly to an acceptable R index of 0.061, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. The refinement procedure included a full-matrix least-squares treatment of coordinates, anisotropic temperature factors, and scale factor. The quantity minimized by the least-squares procedure was $\Sigma w(F_o^2 - F_c^2)^2$ where $w = 1/\sigma^2(F_o^2)$. Hydrogen positions were calculated and added to the structure factor calculation in the latter stages of refinement. Hydrogen parameters were not refined. During the final cycles of refinement the coordinates were contained in one matrix; the anisotropic temperature factors and scale factor, in a second matrix.

Table VI. Intermolecular Close Contacts

Atoms	Hydrogen location	Symmetry operation (on first atom)	Distance, Å
S(2), H(40)	C(15)	$x - 0.5, 0.5 - y, z - 0.5$	2.93
S(3), H(45)	C(18)	$x - 0.5, 0.5 - y, z + 0.5$	2.86
S(11), H(58)	C(28)	$0.5 - x, y + 0.5, 0.5 - z$	2.92
S(12), H(32)	C(7)	$x + 0.5, 0.5 - y, z - 0.5$	2.94
S(20), H(41)	C(16)	$x - 0.5, 0.5 - y, z - 0.5$	2.79
S(20), H(39)	C(15)	$0.5 - x, y - 0.5, z - 0.5$	2.80
S(21), H(33)	C(8)	$x + 1.0, y, z$	2.97
S(21), H(31)	C(7)	$1.0 - x, 1.0 - y, -z$	2.93
C(9), H(46)	C(18)	$x - 1.0, y, z$	3.10
C(13), H(58)	C(28)	$0.5 - x, y + 0.5, 0.5 - z$	3.08
C(24), H(31)	C(7)	$1.0 - x, 1.0 - y, -z$	2.88
C(26), H(36)	C(9)	$0.5 - x, y - 0.5, 0.5 - z$	2.88

Discussion of Crystallographic Results

The final coordinates and anisotropic temperature factors for the nonhydrogen atoms with their standard deviations, calculated from the least-squares residuals and the inverse matrix of the final least-squares cycle, are given in Tables II and III. The shifts calculated for the parameters in the final cycle of least-squares refinement were all less than one-third of the corresponding standard deviations. A final difference Fourier revealed no missing or misplaced atoms. Intramolecular distances and angles are given in Tables IV and V. See Figure 7 for atom labels of Tables I-IV. Positional uncertainties for the nonhydrogen atoms are as follows: C, 0.015 Å; N, 0.009 Å; S, 0.003 Å; In, 0.0007 Å. The standard deviations for individual bonds and angles are given in the appropriate tables. Intermolecular close contacts are given in Table VI. While the distances in Table VI are slightly within van der Waals radii, there are no strong indications that the molecule is distorted by crystal forces.[29]

Registry No. In(pmtc)$_3$, 38560-47-3.

---

(23) D. J. Duchamp, Abstracts, Annual Meeting of the American Association of Crystallographers, Bozeman, Mont., 1964, Paper B-14, p 29.

(24) A. J. C. Wilson, *Nature (London)*, 150, 152 (1942).

(25) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1968, p 202.

(26) R. F. Stewart, R. E. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(27) D. T. Cromer and J. B. Mann, Report LA-3816, Los Alamos Scientific Laboratory, Los Alamos, N. Mex., 1967.

(28) See ref 25, p 216.

(29) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-1347.