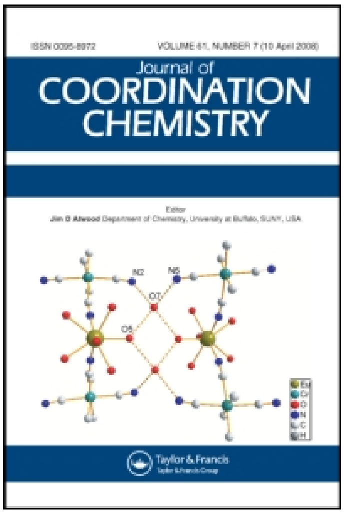

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# Preparation and Reactivity of Planar Trigonal Copper(I) Compounds. Crystal Structure of Bis(2-Thioxohexamethyleneimine)Copper(I) Bromide

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# PREPARATION AND REACTIVITY OF PLANAR TRIGONAL COPPER(I) COMPOUNDS. CRYSTAL STRUCTURE OF BIS(2-THIOXOHEXAMETHYLENEIMINE)COPPER(I) BROMIDE

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The crystal and molecular structure of bis(2-thioxohexamethyleneimine)copper(I) bromide, Cu(tclH)$_2$Br, is reported. The compound is a three-coordinate monomer and crystallizes in space group $P2_1/n$ with $a = 8.807(1)$, $b = 15.893(1)$, $c = 12.385(1)$ Å, $\beta = 105.98(1)°$ and $Z = 4$. It is symmetrically folded with respect to the Cu–Br bond, the copper atom being slightly elevated (0.036 Å) relative to the plane defined by the two sulfur and one bromine donor atoms. The two equivalent Cu–S bonds are 2.228(2) Å and the Cu–Br bond distance is 2.385(1) Å, the interbond angles around copper being close to 120°. Its reactivity towards small molecules (*e.g.*, $CS_2$, $CO_2$) and Lewis bases (*e.g.*, pyridine, $PPh_3$, $AsPh_3$), has also been investigated.

**Keywords:** Copper(I), lactam, X-ray structure, reactivity

## INTRODUCTION

One of the most interesting features of copper(I) is its protean, stereochemistry and possibilities of tuning stereoelectronic factors controlling it, aimed at representation of active enzymic sites.[1] Indeed, copper is second only to iron in occurrence in natural redox systems. Along this line, we have studied the coordination to copper(I) sites[2] of thiones possessing an $\alpha$-nitrogen hereroatom, in an attempt to model thionucleocides and thioaminoacids, which have in several cases been found to coordinate to copper atoms. Particular emphasis has been placed on the determination of the stereochemistry of the metal centre and the coordination mode adopted by the ligands. Recently, we initiated an investigation of the bonding mode of 2-thioxohexamethyleneimine ($\omega$-thiocaprolactam, tclH)[3], as cited in preliminary reports.[4] This bulky thione offers a saturated flexible backbone in contrast to our previous investigations involving compact planar thione molecules. The results of this study are presently described.

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# EXPERIMENTAL

## *Materials and Measurements*

All solvents used were of reagent grade. Copper bromide (BDH) was used without purification, while $\omega$-thiocaprolactam (Aldrich) was recrystallized from hot methanol. Elemental analyses were carried out on a Perkin-Elmer 240 B element analyzer. IR spectra were recorded in KBr discs on a Perkin-Elmer 1430 spectrophotometer, while electronic spectra were obtained by means of a Shimadzu 160 A spectrophotometer. A Bruker AW-80 spectrometer was used for recording $^1$H NMR spectra. The chemical shifts obtained in deuterated chloroform solutions are given ($\delta$, ppm) downfield from internal TMS standard. A Varian FT 20 spectrometer was used for recording $^{13}$C NMR spectra

## *Synthesis*

Reaction of CuBr with excess thione (1:3 molar ratio) was carried out in methanol, with moderate heating for about 15 min. The clear solution was allowed to cool and a white precipitate formed. Its analysis was satisfactory for $Cu(tclH)_2Br$ (calc.: C, 35.86; H, 5.52; N, 6.97%; found: C, 35.27; H, 5.48; N, 6.74%). Slow evaporation of a 1:1 $CH_3OH$:$CHCl_3$ solution of the complex at room temperature produced crystals suitable for X-ray diffraction studies.

## *Solution of the structure*

Crystallographic data and details of data collection and refinement are listed in Table I. Reference reflections showed a loss of intensity of about 2.6%. A correction to the intensities was applied. Data reduction was performed by the Enraf-Nonius SDP/VAX package;[5] Lorentz and polarization effects corrections were performed and an absorption correction was applied based on a $\Psi$-scan of the reflections 012, 013, 014, 025 and 026. Minimum transmission was 0.82. The structure was solved by direct methods, using SHELX-86.[6] Copper scattering factors and anomalous dispersion values were taken from International Tables for Crystallography,[7] while for other atoms the scattering factors were those included in SHELX-76.[8]

The H-atoms were located by a difference Fourier map. The structure was refined by a full-matrix least-squares method;[9] non-H atoms were refined anisotropically and H atoms with isotropic thermal parameters. Drawings were prepared by the PLUTO program as implemented in the SDP package.[5] Calculations were carried out on a MICROVAX II in the X-Ray Laboratory of the Rudjer Boskovic Institute, Zagreb. Final atomic coordinates are listed in Table II.

# RESULTS AND DISCUSSION

## *Description of the structure*

The molecular structure of the monomer is shown in Figure 1 and selected bond lengths and angles are listed in Table III. The figure reveals a three coordinate copper centre, the coordination sphere consisting of two tclH ligands and a bromine atom.

The compound is symmetrically folded with respect to the Cu–Br bond, which is 2.385(1) Å. This bond length is appreciably shorter than those reported for cubane-like

TABLE I

Summary of crystal and intensity collection data.

| | |
|---|---|
| Formula | $CuBrS_2N_2C_{12}H_{22}$ |
| fw | 401.89 |
| $a$(Å) | 8.807(1) |
| $b$(Å) | 15.893(1) |
| $c$(Å) | 12.385(1) |
| $\beta$(deg) | 105.98(1) |
| $V$(Å$^3$) | 1666.5(3) |
| $Z$ | 4 |
| $D_{calcd}$(Mg m$^{-3}$) | 1.602 |
| Space group | $P2_1/n$ |
| Crystal dimensions (mm) | 0.3 × 0.4 × 0.5 |
| Linear absorption coefficient (cm$^{-1}$) | 39.17 |
| $F$(000) | 816 |
| Radiation | Cu K$\alpha$ (graphite monochromator) |
| Temperature (K) | 297 ± 1 |
| $\theta$ range (deg) for cell detn. | 7–12 |
| No. of reflections for cell detn. | 25 |
| $\theta$ min, max | 2, 25 |
| $\omega/2\theta$ scan (A) | $\Delta\omega = 0.80 + 0.35 \tan\theta$ |
| $hkl$ limits | $0 \rightarrow 10$, $0 \rightarrow 18$, $-14 \rightarrow 14$ |
| Reflections collected | 3260 |
| Reflections with $I > 2\sigma(i)$ | 1667 |
| No. of refined parameters | 253 |
| Weighting scheme $\Sigma w\|\|F_0\| - \|F_c\|\|^2$ | $1/w = \sigma^2(F_0) + 0.0007F_0^2$ |
| $R$, $R_w$ | 0.033, 0.035 |

TABLE II

Final atomic coordinates and equivalent isotropic thermal parameters ( × 10$^4$).

| | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$(Å)$^2$ |
|---|---|---|---|---|
| Br | 0.1488(1) | 0.0929(0) | 0.0830(1) | 698(3) |
| Cu | 0.4118(1) | 0.1008(0) | 0.2027(1) | 523(3) |
| S1 | 0.5649(2) | −0.0132(1) | 0.2301(1) | 632(6) |
| S2 | 0.5064(2) | 0.2237(1) | 0.2788(1) | 591(5) |
| N1 | 0.3633(7) | −0.0774(3) | 0.0504(5) | 592(23) |
| C1A | 0.4955(7) | −0.0861(3) | 0.1291(5) | 554(24) |
| C2A | 0.5904(10) | −0.1648(4) | 0.1308(8) | 793(36) |
| C3A | 0.5023(11) | −0.2442(4) | 0.1470(8) | 901(44) |
| C4A | 0.3799(13) | −0.2770(5) | 0.0456(9) | 1083(55) |
| C5A | 0.2439(11) | −0.2176(4) | −0.0039(7) | 848(41) |
| C6A | 0.2911(11) | −0.1349(4) | −0.0420(6) | 696(30) |
| N2 | 0.2573(6) | 0.2924(3) | 0.1377(4) | 532(21) |
| C1B | 0.3849(7) | 0.3038(3) | 0.2191(4) | 454(21) |
| C2B | 0.4268(10) | 0.3920(3) | 0.2594(5) | 616(25) |
| C3B | 0.4670(10) | 0.4496(4) | 0.1734(7) | 727(32) |
| C4B | 0.3241(11) | 0.4842(4) | 0.0872(7) | 771(35) |
| C5B | 0.2179(10) | 0.4185(4) | 0.0145(6) | 705(29) |
| C6B | 0.1466(8) | 0.3567(4) | 0.0789(6) | 623(25) |

$U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$.

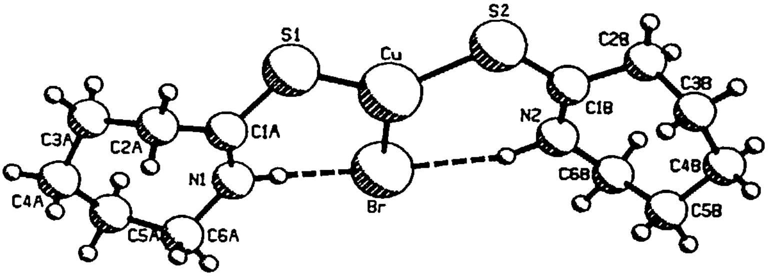

FIGURE 1 A PLUTO drawing of the Cu(tclH)$_2$Br molecule with the atom numbering. Intramolecular hydrogen bonds are denoted by dashed lines.

TABLE III
Interatomic distances (Å) and bond angles (°).

| | | | |
|---|---|---|---|
| Br–Cu | 2.385(1) | Br–Cu–S1 | 119.7(0) |
| Cu–S1 | 2.228(2) | Br–Cu–S2 | 119.7(1) |
| Cu–S2 | 2.228(2) | S2–Cu–S1 | 120.6(1) |
| S1–C1A | 1.691(5) | Cu–S2–C1B | 110.8(2) |
| S2–C1B | 1.696(5) | Cu–S1–C1A | 111.4(2) |
| N1–C1A | 1.304(8) | C1A–N1–C6A | 128.6(5) |
| N1–C6A | 1.466(9) | S1–C1A–N1 | 123.2(4) |
| C1A–C2A | 1.501(9) | N1–C1A–C2A | 118.6(6) |
| C2A–C3A | 1.523(11) | S1–C1A–C2A | 118.3(5) |
| C3A–C4A | 1.505(13) | C1A–C2A–C3A | 113.0(7) |
| C4A–C5A | 1.516(12) | C2A–C3A–C4A | 116.8(7) |
| C5A–C6A | 1.494(10) | C3A–C4A–C5A | 115.2(7) |
| N2–C1B | 1.299(7) | C4A–C5A–C6A | 114.7(8) |
| N2–C6B | 1.461(8) | N1–C6A–C5A | 113.6(6) |
| C1B–C2B | 1.500(7) | C1B–N2–C6B | 127.2(5) |
| C2B–C3B | 1.518(11) | S2–C1B–N2 | 122.7(4) |
| C3B–C4B | 1.512(11) | N2–C1B–C2B | 118.0(5) |
| C4B–C5B | 1.521(10) | S2–C1B–C2B | 119.3(4) |
| C5B–C6B | 1.507(11) | C1B–C2B–C3B | 114.4(5) |
| | | C2B–C3B–C4B | 113.9(7) |
| | | C3B–C4B–C5B | 115.2(6) |
| | | C4B–C5B–C6B | 114.3(6) |
| | | N2–C6B–C5B | 113.7(6) |

cores of formula [CuBrPR$_3$]$_4$[10] or tetrahedral monomers,[11] which vary from 2.51(1) Å for (3,5-dimethylpyridine)$_2$CuBr to 2.599(2) Å for [CuBrP(*t*-Bu)$_3$]$_4$. It is close to the terminal Cu–Br distance of 2.319(2) Å observed in [NEt$_4$]$_2$[Cu$_2$Br$_4$][12] and exceeds the corresponding bond lengths in linear CuBr$_2^-$ units, *e.g.*, in [PEtPh$_3$][CuBr$_2$] and [PPh$_4$][CuBr$_2$],[13] which range from 2.207(2) Å to 2.224(2) Å, respectively.

The two Cu–S bond lengths are identical, 2.228(2) Å. They are in close agreement with several trigonal Cu(I) systems, *e.g.*, Cu(diditme)$_2$Cl,[14] where diditme = *N*,*N*′-dimethylimidazolidine-2-thione, and bis(2-thiouracil)chlorocopper(I)·dmf,[15]

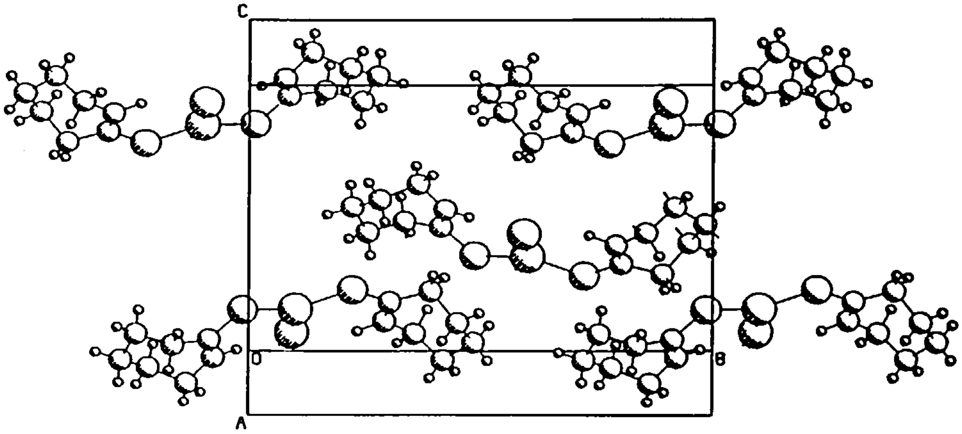

FIGURE 2 Molecular packing in the crystal.

while they slightly exceed those reported for Cu(tetrahydro-1H-pyrimidine-2-thione)$_2$Cl,[16] Cu(*N*-ethyl-1,3-imidazolidine-2-thione)$_2$Cl[17] and Cu{1-phenyl-3-(2-pyridyl)-2-thiourea}$_2$Cl[18] (2.206(2) to 2.218(2) Å). The two S-Cu-Br angles are both equal to 119.7°, thus giving rise to a totally symmetric chromophore; the N-C-S-Cu torsion angles are $-4.2(6)$ and $-1.9(5)$°, respectively.

The intramolecular hydrogen bonds N1-H...Br (N1...Br, 3.388(6) Å, H...Br, 2.379(4) Å, Br-H-N, 178(3)°) and N2-H...Br (N2...Br, 3.327(5) Å, H...Br, 2.369(4) Å, Br-H-N, 157(4)°) provide additional stabilization to the overall conformation, as has been found to be the case in analogous complexes.[3] In the crystal lattice the molecules are held by Van der Waals interactions as shown in Figure 2.

A slight elevation (0.036 Å) of the copper atom relative to the rest of the chromophore is observed, lying within the range observed in trigonal planar or elongated trigonal bipyramidal copper(I) coordination spheres. Finally, the ligand is in a chair conformation with puckering parameters for both rings, Q = 0.742(9) and 0.755(7) Å and $\Theta = 33.6(8)$ and 32.9(6)°, respectively.

### *Spectroscopic and reactivity study*

The IR spectrum of the title compound offers further evidence concerning the coordination mode of the ligand, which occurs exclusively *via* the exocyclic sulfur atom; the characteristic NH stretching vibration is observed at 3150 cm$^{-1}$. The shift of this band relative to that observed in the free thione (3195 cm$^{-1}$) indicates significant intramolecular hydrogen bonding, as confirmed by the structural study. The electronic spectrum in methanol is dominated by a strong band at 277 nm, accompanied by a shoulder at 308 nm. The latter must be attributed to a MLCT excitation, since no analogous absorption is present in the spectrum of the free ligand. The $^1$H NMR spectrum is ientical to that already reported.[4]

Upon treatment with equimolar amounts of NaOH or NaHCO$_3$ in methanol, the compound reacts forming an orange solid, which was formulated as [Cu(tcl)]$_x$ on the basis of elemental analysis, its IR comparison against an authentic sample, formed by the reaction of CuBr with thiocaprolactam (sodium salt) at a 1:1 molar ratio.

It is clear that bulky ligands like tclH "crowd" the metal environment, thus giving rise to low coordination numbers; it seemed interesting though to investigate the extent of this crowding effect by forcing reactions of the complex with several small molecules as well as some Lewis base. The results of these studies are presently discussed.

The title complex is readily soluble in $CS_2$. After stirring for 15 min at ambient temperature the solution was evaporated under reduced pressure to a third of its original volume, and was then allowed to further evaporate at room temperature. IR, $^1H$ NMR and electronic spectra of both the solution and the final solid product indicate that carbon disulfide is bound reversibly to the Cu(I) site.

The complex is also readily dissolved in pyridine and a shoulder at 337 nm in the resulting electronic spectrum is indicative of pyridine adduct formation.[19] The $^1H$ NMR spectrum is similar though not identical to that recorded for the title complex (NH proton at 10.25 ppm, carbon protons at 3.47 (m, 2H), 2.93 (m, 2H) and 1.77 ppm (m, 6H), respectively). Slight differences observed may be attributed to a change in the copper electron density induced by the coordination of pyridine. Depression of the pyridine proton signals in the NMR of the isolated product (observed at 7.1–7.3 ppm (m, 5H)) and the aforementioned shoulder in the electronic spectrum are observed after two days at room temperature, thus indicating reversible binding of puridine to the $CuS_2Br$ core.

Reactions of the complex with $PPh_3$ and $AsPh_3$ in mixed $MeOH:CHCl_3$ (1:1) media produce complexes of the formula $Cu(tclH)_2(EPh_3)Br$ or $Cu(tclH)_2(EPh_3)Br$, depending on the molar ratio of the complex *vs* the ligand. Resulting compounds were identified on the basis of elemental analyses and spectroscopic data. They are identical to those prepared using a different route,[3b] though it seems that the title complex and analogues should provide suitable starting materials for their preparation.

Pyridine-2-thione also reacts, with substitution of tclH in the complex, the reaction being complete over a period of several days. The final product was again identified by spectroscopic data and by comparison of its properties with authentic $[Cu(py2SH)_2Br]_2$ samples.

In view of the above results and of the scarcity of Ci(I) monomer reactions with $CO_2$,[20] we were prompted to investigate the 'fixation' of carbon dioxide in the title compound and its iodo counterpart. Chloroform solutions (0.1 M) of the complexes were pressurized with 1 atm of dry $CO_2$ at room temperature for about 20 min, after which solution IR spectra indicated (new bands at 1640, 1265 and 765 $cm^{-1}$) the

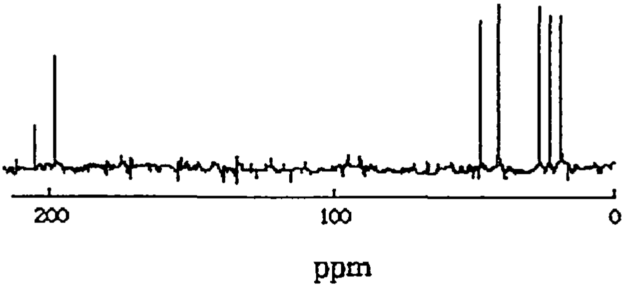

FIGURE 3 $^{13}C$ NMR spectrum of the $Cu(tclH)_2(CO_2)I$ complex.

presence of coordinated $CO_2$ in the case of the iodo compound ($(Cu(tclH)_2Br$ appeared unreacted). Slow evaporation of the former solution produced an amorphous solid with identical characteristic bands in its IR spectrum, recorded in KBr. The close resemblance of this pattern to that reported for a Co-$CO_2$ complex[21] is evidence for $CO_2$ coordination *via* the carbon atom. The coordination of carbon dioxide is further confirmed by the $^{13}C$ NMR of the product, which consists of signals lying close to those reported[4b] for $Cu(tclH)_2X$ ($C_1 = 204.2$, $C_3 = 47.4$, $C_4 = 27.4$, $C_5 = 24.0$, $C_6 = 22.3$ and $C_7 = 43.1$ ppm; atom numbering as in the cited reference) and an additional resonance at 209.8 ppm, ascribed to coordinated $CO_2$ (Figure 3). This dramatic difference in reactivity between the two compounds may be the result of the symmetric chromophore present in the title complex, contrary to its iodo counterpart.

## SUPPLEMENTARY MATERIAL

Tables of fractional coordinates for hydrogen atoms, thermal parameters and observed and calculated structure factors are available from P.K.

### REFERENCES

1. (a) T.N. Sorrell and D.L. Jameson, *J. Am. Chem. Soc.*, **104**, 2053 (1982); (b) M. Pasquali and C. Floriani, in K.D. Karlin and J. Zubieta (Eds.), *Copper Coordination Chemistry, Biochemical and Inorganic Perspectives* (Adenine Press, New York, 1983).
2. (a) P. Karagiannidis, P. Aslanidis, S. Papastefanou, D. Mentzafos, A. Hountas and A. Terzis, *Inorg. Chim. Acta*, **156**, 265 (1989); (b) S.C. Kokkou, S. Fortier, P.J. Rentzeperis and P. Karagiannidis, *Acta Cryst.*, **C39**, 178 (1983).
3. (a) P. Karagiannidis, P.D. Akrivos, D. Mentzafos and A. Hountas, *Inorg. Chim. Acta*, **180**, 93 (1991); (b) P. Karagiannidis, P.D. Akrivos, D. Mentzafos and A. Terzis, *ibid*, **181**, 263 (1991).
4. (a) P. Castan and J. P. Laurent, *C. R. Hebr. Seances Acad. Sci., Ser. C*, **286**, 577 (1978); *C.A.* **89**: 122,221f; (b) P. Castan, *Trans. Metal Chem.*, **6**, 14 (1981).
5. B.A. Frenz, in *Computing in Crystallography*, H. Schenk, R. Olthof-Hazenkamp, H. Van Koningveld and G.C. Bassi (Eds.), (Delft University Press, Holland, 1978), pp.64–71.
6. G.M. Sheldrick, SHELX-86, in *Crystallographic Computing 3*, G.M. Sheldrick, C. Krueger and R. Goddard (Eds.), (Oxford university Press, Oxford, 1985).
7. *International Tables for X-Ray Crystallography*, Vol. IV, J.A. Ibers and W.C. Hamilton (Eds.), (Birmingham, Kynoch Press, 1973).
8. G.M. Sheldrick, *SHELX-77, Program for structure determination* (University of Cambridge, Cambridge, 1983).
9. M. Nardelli, *Comput. Chem.*, **7**, 95 (1983).
10. (a) R.G. Goel and A.L. Beauchamp, *Inorg. Chem.*, **22**, 395 (1983), (b) M.R. Churchill and S.J. Mendak, *ibid.*, **14**, 2041 (1975).
11. J.M. Dyason, L.M. Engelhardt, P.C. Healy and A.H. White, *Aust. J. Chem.*, **39**, 1043 (1986).
12. M. Asplund and S. Jagner, *Acta Chem. Scand.*, **A38**, 135 (1984).
13. S. Andersson and S. Jagner, *Acta Chem. Scand.*, **A39**, 515 (1985).
14. F.A. Devillanova, G. Verani, L.P. Battaglia and A.B. Corradi, *Trans. Metal Chem.*, **5**, 362 (1980).
15. G.W. Hunt, E.A.H. Griffith and E.L. Amma, *Inorg. Chem.*, **15**, 2993 (1976).
16. J.-M. Bret, P. Castan, G. Jugie, A. Dubourg and R. Roques, *J. Chem. Soc., Dalton Trans.*, 301 (1983).
17. L.P. Battaglia, A.B. Corradi, F.A. Devillanova and G. Verani, *Trans. Metal. Chem.*, **4**, 264 (1979).
18. M.B. Ferrari, G.G. Fava, C. Pelizzi and P. Tarasconi, *Inorg. Chim. Acta*, **97**, 99 (1985).
19. S. Kitagawa, M. Munakata and A. Higashie, *Inorg. Chim. Acta*, **59**, 219 (1982).
20. (a) C. Oldham, in G. Wilkinson (Ed.), *Comprehensive Coordination Chemistry*, Vol. 2 (Pergamon, Oxford, 1987), pp450–53; (b) N. Kitajima, K. Fujisawa, T. Koda, S. Hikichi and Y. Moro-oko, *J. Chem. Soc., Chem. Commun.*, 1357 (1990).
21. G. Fachinetti, C. Floriani and P.F. Zanazzi, *J. Am. Chem. Soc.*, **100**, 7405 (1978).