

Terminal and Bridging Pyrazine Ligands in Coordination Polymers Based on Tetrahedral Cu_4OBr_6 Centres

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The polymeric $\text{Cu}_4\text{OBr}_6(\text{pyz})_p(\text{Et}_2\text{O})_r$ complexes *I* ($p = 1.75$, $r = 0.38$), *II* ($p = 2.41$, $r = 0.63$), *III* ($p = 2.65$, $r = 0.48$), *IV* ($p = 3.04$, $r = 0.56$), *V* ($p = 3.52$, $r = 0.53$), and *VI* ($p = 3.95$, $r = 1.00$) in the form of microcrystalline powders have been prepared and the amounts of bridging and terminal pyrazine ligands have been determined from their infrared spectra. These amounts correspond to the related values derived for infinite chains, sheets, and 3D-frameworks based on diamond-like lattice and constructed from the tetrahedral Cu_4OBr_6 centres. The experimental data indicate that the complex *VI* is monomeric, the complex *I* consists of 3D-frameworks, the complexes *II* and *III* can be considered to be mixtures of oligomeric sheets and 3D-frameworks, while the complex *IV* has a chain nature and the complex *V* is dimeric.

Pyrazine is well known to link a variety of coordination centres [1]. The copper(II) coordination centres to be linked by pyrazine mostly prefer square planar coordination which is completed by linking pyrazine in chains [2–5] and sheets [6–10] to square pyramids or octahedra. However, in copper(I) coordination polymers, trigonal [11–13] or tetrahedral [11, 14–16] coordination is preferred.

The coordination polymers built up of tetrahedral copper(I) centres consist of infinite chains [14], infinite sheets [11, 15, 16], and infinite three-dimensional framework with a diamond-like lattice [13]. In two of the sheet structures [11, 16], hexanuclear copper(I) units form a chair-type cyclohexane-like structure. Generally, the tetrahedral coordination centres can be linked by molecular rod-like ligands to infinite diamond-related frameworks [17].

Tetranuclear $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes [18–20] contain a tetrahedral centre based on the central oxygen atom as it is seen in Fig. 1. These complexes provide the tetrahedral copper(II) coordination centres represented by Cu_4OX_6 moieties which can be theoretically linked by rod-like bridging ligands *L* (e.g. pyrazine) to form one-, two- or three-dimensional frameworks.

We present a series of $\text{Cu}_4\text{OBr}_6(\text{pyz})_p(\text{Et}_2\text{O})_r$ (*pyz* = pyrazine) complexes in which the tetrahedral Cu_4OBr_6 centres are linked by pyrazine to various extent which is controlled by the mole ratio of reactants. The amounts of terminal and bridging pyrazine ligands which vary with the extent of polymer growth enable us to present the details of pyrazine infrared spectra. The experimental results on terminal and bridging pyrazine ligands in the $\text{Cu}_4\text{OBr}_6(\text{pyz})_p(\text{Et}_2\text{O})_r$ complexes are compared with the theoretically derived re-

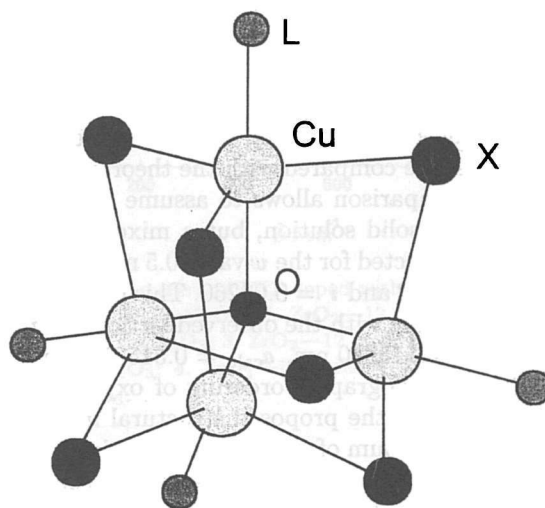


Fig. 1. Structure of tetrahedral Cu_4OX_6 centre in $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes.

lations for linkage of tetrahedral Cu_4OBr_6 centres to construct diamond-like structures.

EXPERIMENTAL

Electronic spectra were measured with a Unicam SP-700C spectrometer. Infrared spectra were recorded with Philips Analytical PU 9800 FTIR and with Nicolet Magna 750 spectrophotometers in Nujol mull and polyethylene matrix.

The absorbances of the bands in infrared spectra were determined by baseline method [21] and processed with Omnic software [22].

The amounts of total pyrazine (p) in the Cu₄OBr₆-(pyz) _{p} (Et₂O) _{r} complexes were calculated from the elemental analysis. The amounts of bridging (b) and terminal (t) pyrazine were calculated from the equations

$$b + t = p \quad (1)$$

$$(A_b/A_t) = (\varepsilon_b/\varepsilon_t)(b/t) \quad (2)$$

The absorbances A_b and A_t were obtained using the bands at $\bar{\nu} = 484 \text{ cm}^{-1}$ and 459 cm^{-1} for bridging and terminal pyrazine ligands, respectively. The value of the molar absorption coefficient ratio $\varepsilon_b/\varepsilon_t = 0.483$ was calculated from measured absorbances and amounts of pyrazine $b = 0.5$ and $t = 3.0$ for the dimer Cu₄OBr₆(pyz)_{3.5}. This value has been considered to be constant for all of the Cu₄OBr₆(pyz) _{p} (Et₂O) _{r} complexes.

Complexes Cu₄OBr₆(pyz) _{p} (Et₂O) _{r}

The complexes were prepared by reaction of the initial Cu₄OBr₆(MeOH)₄ complex and pyrazine. The

initial complex was prepared by refluxing of CuO (1 mmole in excess of 25 %) and CuBr₂ (3 mmole) in 2 cm³ of ether and 0.5 cm³ of methanol for 30 min [23]. After filtration the solution was diluted with 10 cm³ of ether and reacted with pyrazine (dissolved in 2 cm³ of ether) in required mole ratio. Immediately precipitated brown complexes were filtered and washed with 15 cm³ of ether. The synthesis and isolation of the complexes were performed in dried solvents under nitrogen atmosphere.

RESULTS AND DISCUSSION

The composition of the complexes calculated from the data found by elemental analysis is expressed in Table 1. The presence of the tetrahedral coordination centre in the structure of complexes is clearly indicated [24, 25] by the band of the tetrahedral core OCu₄ vibration in the region 536—544 cm⁻¹ and the trigonal bipyramidal coordination of copper(II) atom by a diagnostic [24] $d-d$ band at about 11 500 cm⁻¹ and a shoulder at about 13 000 cm⁻¹. Infrared spectra of the Cu₄OBr₆(pyz) _{p} (Et₂O) _{r} complexes (Fig. 2, Table 2) clearly show that most bands of the fun-

Table 1. Absorbances (A_t , A_b), Amounts of Bridging (b), Terminal (t) and Total (p) Pyrazine Ligands in the Studied Complexes

Complex	Composition	A_t	A_b	b	t	p
I	Cu ₄ OBr ₆ (pyz) _{1.75} (Et ₂ O) _{0.38}	0.006	0.129	1.71	0.04	1.75
II	Cu ₄ OBr ₆ (pyz) _{2.41} (Et ₂ O) _{0.63}	0.146	0.165	1.69	0.72	2.41
III	Cu ₄ OBr ₆ (pyz) _{2.65} (Et ₂ O) _{0.48}	0.211	0.109	1.37	1.28	2.65
IV	Cu ₄ OBr ₆ (pyz) _{3.04} (Et ₂ O) _{0.56}	0.386	0.091	1.00	2.04	3.04
V	Cu ₄ OBr ₆ (pyz) _{3.52} (Et ₂ O) _{0.53}	0.132	0.010	0.48	3.04	3.52
VI	Cu ₄ OBr ₆ (pyz) _{3.95} (Et ₂ O) _{1.00}	0.628	0	0.00	3.95	3.95

Table 2. Vibrational Spectra of the Studied Complexes

Pyrazine	$\bar{\nu}_i/\text{cm}^{-1}$						Assignment ^a
	VI	V	IV	III	II	I	
417	459 vs	459 vs	459 vs	459 vs	459 m	459 vw	ν_{16b} (ring)
	—	484 vw	484 m	484 s	484 s	484 s	
	536 vs	536 vs	538 vs	540 vs	542 vs	544 vs	
804	806 vs	806 vs	806 vs	810 vs	810 vs	812 vs	$\nu(\text{Cu}_4\text{O})$ ν_{11} (H-bend, out of plane)
	843 w	843 w	843 w	843 w	843 w	843 w	
1022	1019 m	1019 w	1019 w	1019 w	1019 vw	—	ν_{12} (ring)
1067	1057 vs	1055 vs	1057 vs	1057 vs	—	—	ν_{18a} (H-bend, in plane)
	—	—	1069 vs	1069 vs	1069 vs	1069 vs	
	1113 sh	1113 sh	1113 vs	1113 sh	—	—	
1148	1123 vs	1123 vs	1123 vs	1123 vs	1123 vs	1123 vs	$\nu(\text{C—O—C})$, Et ₂ O ν_{15} (H-bend, in plane)
	1157 vs	1157 vs	1157 vs	1157 vs	1159 vs	1159 vs	
	1219 m	1219 m	1219 m	1221 w	1221 vw	—	
1418	1229 m	1229 m	1229 m	1229 w	1229 w	1231 w	ν_{19b} (ring)
	1412 vs	1412 s	1412 sh	1412 sh	1412 sh	—	
	1416 vs	1416 vs	1416 vs	1418 vs	1418 vs	1420 vs	
1523	1522 w	1522 w	1522 w	1522 vw	1522 vw	—	ν_{8a} (ring)
1584	1595 m	1595 m	1595 m	1595 w	1611 vw	—	ν_{8b} (ring)

a) Ref. [25].

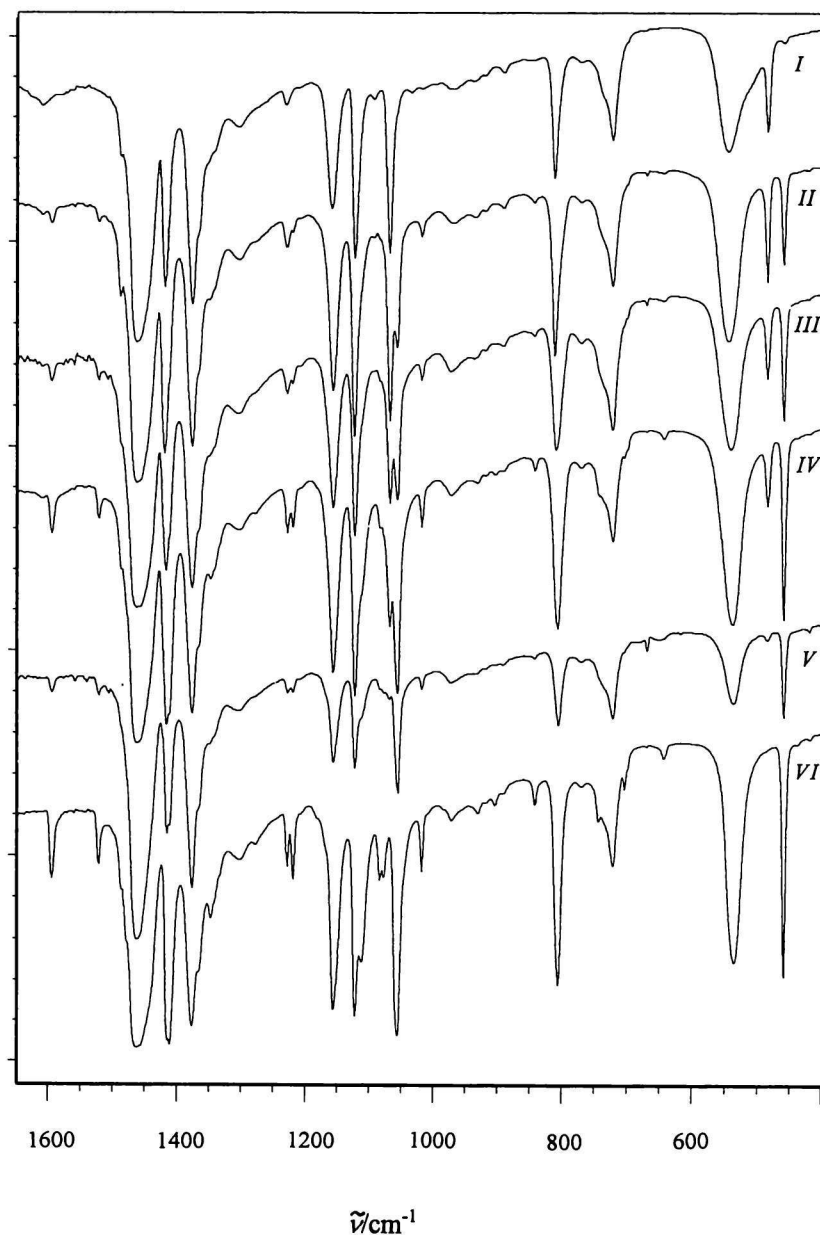


Fig. 2. Infrared spectra of $\text{Cu}_4\text{OBr}_6(\text{pyz})_p(\text{Et}_2\text{O})_r$ complexes.

damental vibrations of pyrazine [26] are shifted as a consequence of its bridging or terminal mode of coordination. The vibration $\tilde{\nu}_{16b}$ with the bands at 459 cm^{-1} and 484 cm^{-1} for bridging and terminal pyrazine ligands, respectively, shows to be the most sensitive to the mode of pyrazine coordination in the $\text{Cu}_4\text{OBr}_6(\text{pyz})_p(\text{Et}_2\text{O})_r$ complexes, which is in accordance with the other findings [5, 8, 14, 27, 28]. These bands are satisfactorily separated and their absorbances can be described by Beer's law. Therefore, they are suitable for determination of bridging and terminal pyrazine ligands in the $\text{Cu}_4\text{OBr}_6(\text{pyz})_p(\text{Et}_2\text{O})_r$ complexes (Table 1).

Changing the mode of the pyrazine coordination from terminal to bridging, the following shifts of se-

lected bands proceed: $806\text{ cm}^{-1} \rightarrow 812\text{ cm}^{-1}$, $1057\text{ cm}^{-1} \rightarrow 1069\text{ cm}^{-1}$, $1157\text{ cm}^{-1} \rightarrow 1159\text{ cm}^{-1}$, and $1416\text{ cm}^{-1} \rightarrow 1420\text{ cm}^{-1}$. These shifts are, however, not significant. The change of pyrazine local symmetry related to the change of pyrazine coordination mode from terminal to bridging corresponds to the disappearing of the relatively weak bands at $\tilde{\nu}/\text{cm}^{-1}$: 843, 1019, 1219, 1523, and 1584.

The $\text{Cu}_4\text{OBr}_6(\text{pyz})_p(\text{Et}_2\text{O})_r$ complexes contain ether solvent molecules as indicated by a strong C—O—C band at 1123 cm^{-1} . This structural type of complexes usually contains molecules of solvents [29, 30], moreover complexes with pyrazine [11, 27] and diamond-related lattices [17] have placed the solvent molecules in cubic or hexagonal cavities. Complex *I*

shows the presence of an impurity which comes from parent Cu₄OBr₆(MeOH)₄ complex (shoulder at the OCu₄ core band and the bands at 3400 cm⁻¹ and 1610 cm⁻¹ of coordinated methanol). Generally, the complexes prepared from the reaction mixture with the low pyrazine concentration are usually contaminated by this impurity. The wavelengths of the OCu₄ core vibration band are tuned by the variation of the terminal and bridging pyrazine ligands. This is indicated by the fine shifts of the OCu₄ core band from 536 cm⁻¹ to 544 cm⁻¹.

The pyrazine copper(I) coordination polymers with the tetrahedral coordination centres showed chains [14], hexagonal sheets [11, 15, 16], and diamond-related lattices [13]. This corresponds to the fact that the tetrahedral centres can be linked to form cycles, chains, sheets, and 3D-frameworks which correspond to analogous structures derived from cubic diamond or hexagonal lonsdaleite lattices [31] when there are favourable steric and electronic conditions for such linkages.

For infinite chains, sheets, and diamond-related 3D-frameworks constructed from the Cu₄OBr₆ tetrahedral coordination centres, the linear relationship (3) (Fig. 3) between the amounts of bridging (*b*) and terminal (*t*) pyrazine ligands can be easily derived since the monomer is composed of O*t*₄b₀, the infinite chain is composed of O*t*₂b₁, the infinite sheet of O*t*₁b_{1.5}, and the infinite 3D-framework of O*t*₀b₂ centres linked by pyrazine (Table 3).

$$b = -0.5t + 2 \quad (3)$$

There are three regions, *a*, *b*, and *c* in Fig. 3 corresponding to oligomers of 3D-frameworks, sheets, and chains, respectively, extending between related elemental chain (O*t*₃b_{0.5}), sheet (O*t*_{2.5}b_{0.75}), and 3D-framework (O*t*_{2.4}b_{0.8}) drawn with thin lines and the edges defined by infinite structures drawn with thick lines (see also Table 3).

The amounts of terminal (*t*) and bridging (*b*) pyrazine molecules calculated using eqn (2) are in good correlation with the straight line describing the structures of the oligomers. It means that the tetrahedral Cu₄OBr₆ centres are linked by pyrazine ligands to form structures derived from diamond-related lattices. Similar structural behaviour showed the frameworks constructed from tetrahedral copper(I) centres [11, 13–16]. The data of Fig. 3 indicate that besides the monomeric complex VI, the complex I is represented by infinitive 3D-framework, the complexes II and III can be considered as mixtures of oligomeric sheets and 3D-frameworks, while the complex IV has a chain nature and the complex V is dimeric.

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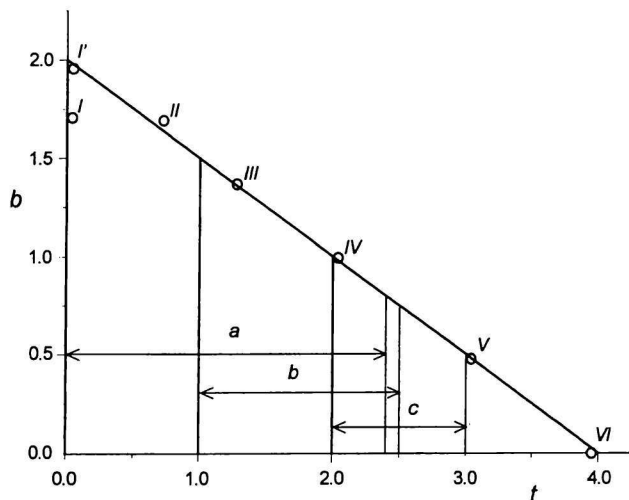


Fig. 3. Linear relationship between the amounts of bridging (*b*) and terminal (*t*) pyrazine ligands in Cu₄OBr₆-(pyz)_{*p*}(Et₂O)_{*r*} complexes. — Theoretical straight line, $b = -0.5t + 2$, ○ experimental values. Data for point I' were obtained by correction of point I for the presence of an admixture (initial complex Cu₄OBr₆(MeOH)₄).

Table 3. Average Composition of Tetrahedral Centres in Polymeric Structures Derived from Diamond-Related Lattices

Structure	Average composition of tetrahedral centres	
	Structural element	Infinite structure
Monomer	O <i>b</i> ₀ <i>t</i> ₄	—
Chain	O <i>b</i> _{0.5} <i>t</i> ₃	O <i>b</i> ₁ <i>t</i> ₂
Sheet	O <i>b</i> _{0.75} <i>t</i> _{2.5}	O <i>b</i> _{1.5} <i>t</i> ₁
3D-Framework	O <i>b</i> _{0.8} <i>t</i> _{2.4}	O <i>b</i> ₂ <i>t</i> ₀

REFERENCES

1. Steel, P. J., *Coord. Chem. Rev.* **106**, 221 (1990).
2. Santoro, A., Mighell, A. D., and Reimann, C. W., *Acta Crystallogr.*, **B 26**, 979 (1970).
3. Belford, R. C. E., Fenton, D. E., and Truter, M. R., *J. Chem. Soc., Dalton Trans.* **1974**, 17.
4. Morosin, B., Hughes, R. C., and Soos, Z. G., *Acta Crystallogr.*, **B 31**, 762 (1975).
5. Fetzer, Th., Lentz, A., and Debaerdemaeker, T., *Z. Naturforsch.* **44b**, 553 (1989).
6. Dariet, J., Haddad, M. S., Duesler, E. N., and Hendrickson, D. N., *Inorg. Chem.* **18**, 2679 (1979).
7. Haynes, J. S., Rettig, S. J., Sams, J. R., Thompson, R. C., and Trotter, J., *Can. J. Chem.* **65**, 420 (1987).
8. Otieno, T., Rettig, S. J., Thompson, R. C., and Trotter, J., *Inorg. Chem.* **32**, 4384 (1993).
9. Kawata, S., Kitagawa, S., Kondo, M., Furuchi, I., and Munakata, M., *Angew. Chem.* **106**, 1851 (1994).

10. Kitagawa, S., Okubo, T., Kawata, S., Kondo, M., Katada, M., and Kobayashi, H., *Inorg. Chem.* 34, 4790 (1995).
11. Kitagawa, S., Munakata, M., and Tanimura, T., *Inorg. Chem.* 31, 1714 (1992).
12. Turnbull, M. M., Pon, G., and Willett, R. D., *Polyhedron* 10, 1835 (1991).
13. Otieno, T., Rettig, S. J., Thompson, R. C., and Trotter, J., *Inorg. Chem.* 32, 1607 (1993).
14. Otieno, T., Rettig, S. J., Thompson, R. C., and Trotter, J., *Can. J. Chem.* 67, 1964 (1989).
15. Moreno, J. M., Suarez-Varela, J., Colacio, E., Avila-Roson, J. C., Hidalgo, M. A., and Martin-Ramos, D., *Can. J. Chem.* 73, 1591 (1995).
16. Halasyamani, P., Heier, K. R., Willis, M. J., and Stern, Ch. L., *Z. Anorg. Allg. Chem.* 622, 479 (1996).
17. Hoskins, B. F. and Robson, R., *J. Am. Chem. Soc.* 112, 1546 (1990).
18. Bertrand, J. A. and Kelley, J. A., *J. Am. Chem. Soc.* 88, 4746 (1966).
19. Bertrand, J. A., *Inorg. Chem.* 6, 495 (1967).
20. Jorík, V., Koman, M., Makáňová, D., Mikloš, D., Broškovičová, A., and Ondrejovič, G., *Polyhedron* 15, 3129 (1996).
21. Horák, M. and Vítek, A., *Zpracování a interpretace vibračních spekter.* (Processing and Interpretation of Infrared Spectra.) P. 269. Nakladatelství technické literatury (Publishers of Technical Literature), Prague, 1980.
22. OMNIC, FTIR Software, Nicolet Analytical Instruments, Madison WI 53711, 1994.
23. tom Dieck, H. and Brehm, H. P. *Chem. Ber.* 102, 3577 (1969).
24. tom Dieck, H., *Inorg. Chim. Acta* 7, 397 (1973).
25. Linert, W., Weinberger, P., Ondrejovič, G., and Makáňová, D., *Vib. Spectrosc.* 5, 101 (1993).
26. Lord, R. C., Marston, A. L., and Millers, F. A., *Spectrochim. Acta* 9, 113 (1957).
27. Goldstein, M. and Unsworth, W. D., *Spectrochim. Acta* 27A, 1055 (1971).
28. Haynes, J. S., Rettig, S. J., Sams, J. R., Trotter, J., and Thompson, R. C., *Inorg. Chem.* 27, 1237 (1988).
29. Makáňová, D. and Ondrejovič, G., *Polyhedron* 8, 2469 (1989).
30. Simonov, Yu. A., Dvorkin, A. A., Yampolskaya, M. A., and Zavodnik, V. E., *Zh. Neorg. Khim.* 27, 1220 (1982).
31. Wells, A. F., *Structural Inorganic Chemistry.* Clarendon Press, Oxford, 1975.

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