Notizen / Notes

A Novel *vic*-Dioxime with Crown Ether Moieties

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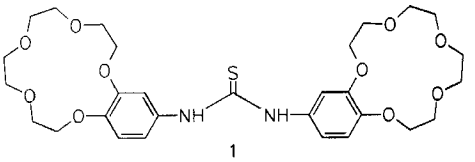
Received December 4, 1989

Key Words: Oxime complexes / Imidazolines / Cobalt complexes / Crown ethers

The novel *vic*-dioxime **2** has been synthesized by reaction of the thiourea **1** with cyanogen *N,N'*-dioxide. The IR and NMR data indicate that **2** is the (*E,Z*) isomer. However, in the Co(III) complex of **2**, the metal ion is coordinated to the nitrogen atoms of the *vic*-dioxime moiety as in the case of the (*E,E*) isomers.

Bis(crown ethers) have been found to be powerful extracting agents for alkali metal salts[1,2]. They are also accepted to be model compounds to mimic antibiotics in cation transport through lipid membranes[3,4]. Addition of crown ether substituents to various coordination compounds causes an increase in their solubility in common organic solvents and in water[5]. These studies suggest that a suitable combination of the crown ether unit with other donor groups may provide a possibility for preparing new functionalized materials. In this note, we report on the synthesis and properties of a new heterocyclic *vic*-dioxime bearing crown ether moietics and on its Co(III) complex.



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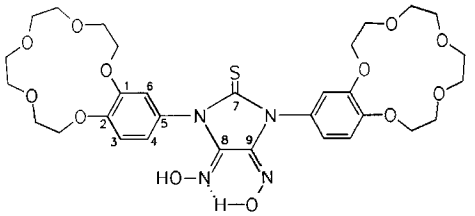
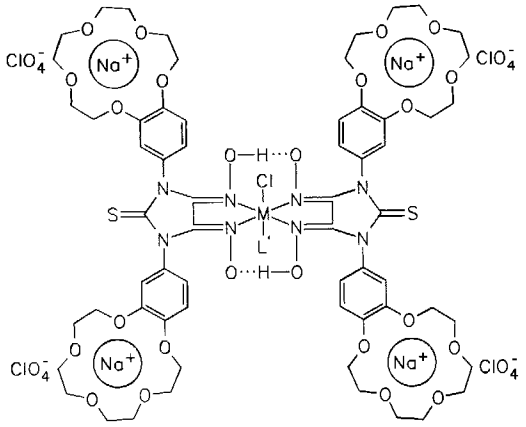


2



3 (L = benzimidazole)

The *vic*-dioxime **2** is synthesized from **1** and cyanogen *N,N'*-dioxide. The high solubility of **2** in polar solvents such as ethanol, acetone, or DMF should be mentioned. In the ^{1}H-NMR spectrum of **2**, two with deuterium exchangeable protons at δ = 9.50 and 10.60 have been observed. Since in symmetrically substituted *vic*-dioximes, (*E,E*) and (*Z,Z*) configurations have equivalent oxime protons, these two signals should correspond to the free (δ = 9.50) and hydrogen-bonded (δ = 10.60) OH groups of the (*E,Z*) isomer[6,7]. This structure is confirmed by two different signals for C-8 and C-9 observed in the ^{13}C-NMR spectrum[8,9]. In the IR spectrum, the broad absorption at $\tilde{\nu}$ = 3180 cm^{-1} can be assigned to OH stretching vibrations and the other two absorptions at $\tilde{\nu}$ = 1675 and 1560 cm^{-1} to the C=N stretching vibrations of the (*E,Z*) configuration[10-12].

The Co(III) complex is prepared similarly to that of dimethylglyoxime[13]. The axial ligand in this octahedral complex **3** is benzimidazole. The structure of this diamagnetic compound has been elucidated on the basis of IR and ^{1}H-NMR data. The weak band assigned to the intramolecular bending vibration of the O−H··O bond is observed at $\tilde{\nu}$ = 1700 cm^{-1}. The complex exhibits a ν(C=N) absorption at $\tilde{\nu}$ = 1625 cm^{-1}. In the ^{1}H-NMR spectrum of **3**, the O−H··O protons appear as a singlet at δ = 17.6, which disappears by D_2O exchange. The shift of the OH proton signals to lower field in the ^{1}H-NMR spectrum and the characteristic absorptions in the IR spectrum suggest that in **3** the (*E,E*) isomer of **2** is present. Since the (*E,E*) isomer is the most stable one[7], this conversion can occur during complex formation.

This work has been supported by the *Research Fund of Karadeniz Technical University* (Trabzon, Turkey). The authors are indebted to Prof. Dr. *Ö. Bekaroğlu* (İstanbul, Turkey) for valuable discussions.

Experimental

IR (KBr): Perkin-Elmer 583. – UV-VIS: GBC 911. – ^{1}H, ^{13}C NMR: Bruker AC (200 MHz). – MS: Varian MAT 711. – Elemental analyses: Perkin-Elmer 240 C [TÜBİTAK Research Institute for Basic Science (Gebze, Turkey)]. – Benzo-15-crown-5[1] has been prepared according to a literature procedure.

Synthesis of **1** · KCl: A solution of thiocarbonyl dichloride (1.15 g, 10 mmol) in absolute ethanol (20 ml) was added to a solution of

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4′-aminobenzo-15-crown-5[14,15] (5.66 g, 20 mmol) and K_2CO_3 (1.38 g, 10 mmol) in absolute ethanol (180 ml) at −10°C. The mixture was stirred continuously at this temp. for 5 h. The white precipitate was filtered off, washed with absolute ethanol and dry diethyl ether, and then dried in vacuo; yield 6.11 g (90%), m.p. 224°C. – IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1} (NH), 3040 ($CH_{arom.}$), 1245–1220 (Ar–O–C), 1180–1120 (C–O–C). – UV-VIS (ethanol/water): λ_{max} (lg ε) = 251 nm (4.24), 275 (4.18), 312 (4.47), 352 (3.21). – ^{1}H NMR ([D$_6$]DMSO): δ = 4.03–3.33 (m, 32H, CH_2O), 6.89–6.85 (m, 6H, Ar–H), 7.88 (s, 2H, NH).

$C_{29}H_{40}N_2O_{10}S \cdot KCl$ (682.5)
Calcd. C 50.98 H 5.86 N 4.10 K 5.71
Found C 50.70 H 5.62 N 3.88 K 5.56

Preparation of **1**: **1** · KCl (6.0 g, 8.79 mmol) was dissolved in water (225 ml) and extracted with chloroform (225 ml). The solution was dried with anhydrous $MgSO_4$ and then evaporated to dryness under vacuum. The white product was dried in vacuo; yield 4.29 g (80%), m.p. 106°C. – IR (KBr): $\tilde{\nu}$ = 3340 cm^{-1} (NH), 3045 ($CH_{arom.}$), 1240–1210 (Ar–O–C), 1180–1130 (C–O–C). – UV-VIS ($CHCl_3$): λ_{max} (lg ε) = 263 nm (4.76), 276 (4.64), 316 (4.56), 352 (3.77). – ^{1}H NMR ($CDCl_3$): δ = 4.12–3.57 (m, 32H, CH_2O), 6.98–6.82 (m, 6H, Ar-H), 7.64 (s, 2H, NH). – ^{13}C NMR ($CDCl_3$): δ = 70.9–69.3 (CH_2O), 180.5 (C=S). – MS (70 eV): *m/z* (%) = 608 (38) [M^+].

$C_{29}H_{40}N_2O_{10}S$ (608.4) Calcd. C 57.23 H 6.57 N 4.60
Found C 56.98 H 6.41 N 4.38

Synthesis of **2**: **1** (3.648 g, 6 mmol) was dissolved in dichloromethane (50 ml) and cooled to −10°C. A solution of cyanogen *N,N′*-dioxide[16,17] [prepared from (*E,E*)-dichloroglyoxime[16] (0.942 g, 6 mmol) and 0.5 M aqueous Na_2CO_3 solution (30 ml) at −10°C] in dichloromethane (30 ml) was added to the solution of **1**. The reaction was continued for a further 10 h at this temp. and then warmed to 0°C. **2** was precipitated by the addition of diethyl ether with continous stirring. The pale-yellow precipitate was recrystallized in 300 ml of ethanol/petroleum ether (1:4). The pale-yellow needles were filtered off, washed with cold ethanol, and then dried in vacuo; yield 2.30 g (55%), m.p. 141°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3180 cm^{-1} (OH), 3040 ($CH_{arom.}$), 1675, 1560 (C=N), 1240–1220 (Ar–O–C), 1170–1120 (C–O–C), 940 (NO). – UV-VIS (CH_2Cl_2): λ_{max} (lg ε) = 260 nm (4.26), 320 (3.32), 345 (3.08). – ^{1}H NMR ([D$_6$]DMSO): δ = 4.02–3.38 (m, 32H, CH_2O), 7.18–6.86 (m, 6H, Ar-H), 9.50–10.60 (s, 2H, OH). – ^{13}C NMR ([D$_6$]DMSO): δ = 70.3–68.3 (CH_2O), 148.7 (C-9), 152.8 (C-8), 180.1 (C-7).

$C_{31}H_{40}N_4O_{12}S$ (692.4) Calcd. C 53.75 H 5.78 N 8.09
Found C 53.57 H 5.62 N 7.81

Synthesis of **3**: A solution of $CoCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol) in ethanol (25 ml) was added to a solution of **2** (1.38 g, 2 mmol) in ethanol (50 ml). The mixture was heated with stirring to 60°C. Then a solution of benzimidazole (0.78 g, 6.6 mmol) in ethanol (25 ml) was added, and O_2 was bubbled through the mixture for 30 min. A satd. solution of $NaClO_4$ in ethanol (7 ml) was added to this solution. The dark-brown precipitate was removed by filtration, washed succesively with dichloromethane, cold ethanol, and dry diethyl ether, and then dried in vacuo; yield 1.64 g (79%), m.p. 229°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1} ($CH_{arom.}$), 1700 (O–H··O), 1625 (C=N), 1240–1220 (Ar–O–C), 1150–1040 (ClO_4^-), 940 (NO). – UV-VIS (DMF): λ_{max} (lg ε) = 265 nm (4.69), 275 (4.65), 295 (4.04), 355 (4.38), 515 (3.38). – ^{1}H NMR ([D$_6$]-DMSO): δ = 4.03–3.65 (m, 64H, CH_2O), 7.18–6.88 (m, 12H, Ar-H), 17.60 (s, 2H, O–H··O).

$C_{69}H_{84}ClCoN_{10}O_{24}S_2 \cdot 4NaClO_4$ (2084.9)
Calcd. C 39.72 H 4.03 N 6.71 Co 2.82
Found C 39.60 H 3.79 N 6.52 Co 2.58

CAS Registry Numbers

1: 126541-42-2 / **1** (K Complex) · Cl^-: 126504-66-3 / **2** (*E,Z*): 126504-63-0 / **3**: 126504-65-2 / 4′-aminobenzo-15-crown-5: 60835-71-4

[1] C. J. Pedersen, *J. Am. Chem. Soc.* **89** (1967) 7033.
[2] A. V. Bajaj, N. S. Poonia, *Coord. Chem. Rev.* **87** (1988) 55.
[3] S. Shinkai, M. Ishihara, K. Ueda, O. Manabe, *J. Chem. Soc., Perkin Trans. 2*, **1985**, 511.
[4] T. Minami, S. Shinkai, O. Manabe, *Tetrahedron Lett.* **23** (1982) 5167.
[5] A. Gül, Ö. Bekaroğlu, *J. Chem. Soc., Dalton Trans.* **1983**, 2537.
[6] A. Daniel, A. A. Pavia, *Tetrahedron Lett.* **13** (1967) 1145.
[7] S. B. Pedersen, E. Larsen, *Acta Chem. Scand.* **27** (1973) 3291.
[8] R. L. Lichter, D. E. Dorman, R. Wasylishen, *J. Am. Chem. Soc.* **96** (1974) 930.
[9] M. S. Gordon, S. A. Sojka, J. G. Krause, *J. Org. Chem.* **49** (1984) 97.
[10] M. Erbaş, A. R. Koray, V. Ahsen, Ö. Bekaroğlu, *J. Organomet. Chem.* **319** (1987) 197.
[11] A. Nakamura, A. Konishi, S. Otsuka, *J. Chem. Soc., Dalton Trans.* **1978**, 488.
[12] M. S. Ma, R. J. Angelici, *Inorg. Chem.* **19** (1980) 363.
[13] G. N. Schrauzer, J. Kohnle, *Chem. Ber.* **97** (1964) 3056.
[14] R. Ungaro, B. E. Haj, J. Smid, *J. Am. Chem. Soc.* **98** (1976) 5198.
[15] E. Shchori, J. Jagur-Grodzinski, M. Shporer, *J. Am. Chem. Soc.* **95** (1973) 3842.
[16] G. Ponzio, F. Baldrocco, *Gazz. Chim. Ital.* **60** (1930) 415.
[17] C. Grundmann, V. Mini, S. M. Dean, H. D. Frommeld, *Liebigs Ann. Chem.* **687** (1965) 191.

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