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Phenylenedioxydiacetamide—End Group Effect[1]

Short Communication

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A series of neutral ligands featuring ether and amide groups were prepared. The complexation studies suggest a strong participation of the extra terminal amide group.

(Keywords: Complexation studies; Neutral ionophoros; Neutral ligands)

Phenylendioxyacetamid-Endgruppen Effekt (Kurze Mitteilung)

Es wurde eine Reihe neutraler Liganden mit Ether- bzw. Amid-Gruppierungen hergestellt. Untersuchungen des Komplexierungsverhaltens legt eine sehr starke Beteiligung der zusätzlichen Amid-Endgruppen nahe.

Recent studies have shown that noncyclic, uncharged neutral ligands like ethylenedioxydiacetamides are able to complex alkali and alkali earth metal cations[2]. We wish to report here a synthesis of a series of phenylenedioxydiacetamides together with preliminary complexation studies.

Catechol in the presence of sodium hydroxide in water reacts with ethyl chloroacetate (room temperature, two hours) to afford, after recrystallization (HCl—water), phenylenedioxydiacetic acid in 55% yield. Reacting this diacid with thionyl chloride at reflux for two hours affords phenylenedioxydiacetyl chloride, which then condenses with the appropriate amine in the presence of triethyl amine in benzene to give the free ligands **3**.

The complexation studies were carried out by a.) direct UV titraction measurement and b.) picrate extraction method. These studies show that these ligands do not complex monovalent cations but complex well with the Group II A cations. The ligands **3 b-c** show the chelation capacity to more less the same extent as it in **3 a**. This

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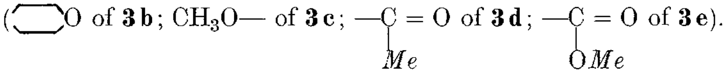
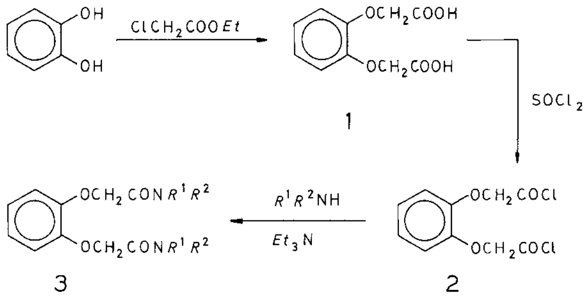
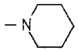
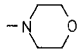
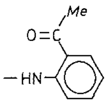
information suggests that the participation of the terminal oxygen atom is a minimum

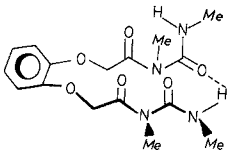


(O of **3b**; CH_3O— of **3c**; —$\underset{Me}{C}$ = O of **3d**; —$\underset{OMe}{C}$ = O of **3e**).

In comparison with **3a–e**, compound **3f** shows a much stronger complexation power with divalent cations, especially Ca^{++} (at ligand/picrate = 10, **3f** extracts 40% picrate which is more than double as for **3a–e**). A crystalline complex of **3f** with $Ca(SCN)_2$ was isolated with 1:1 stoichiometry. (**3f**: $C_{16}H_{22}N_4O_6$; calc. C 52.45, H 6.05, N 15,29; found, C 52.19, H 6.05, N 15.29. **3f**·$Ca(SCN)_2$; Calc. C 41.38, H 4.21, N 16.16; found, C 41.35, H 4.25, N 16.20). This could be explained by a



3	$-NR^1R^2$
a	
b	
c	$-NHCH_2CH(OMe)_2$
d	
e	$-NHCMe{=}CHCOOMe$
f	$-NMeCONHMe$



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possible intramolecular hydrogen bonding to form a more rigid structure (**4**) to increase the complexation capacity and this also suggests the possible participation of the terminal carbonyl group in complexation.

Acknowledgement

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References

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[2] a) *Amann, D.*, *Bissig, R.*, *Güggi, M.*, *Pretsch, E.*, *Simon, W.*, *Borowitz, I. J.*, *Weiss, L.*, Helv. Chim. Acta **58**, 1535 (1957); b) *Borowitz, I. J.*, *Lin, W. O.*, *Wun, T. C.*, *Bittman, R.*, Tetrahedron **33**, 1697 (1977).