

New Xylylene Bis (dithiocarbamates) as a Solvent Extractor

Satsuo KAMATA*, Hiroki KUSUMOTO* and Keniti SODEYAMA**

New noncyclic xylylene bis (dialkyl / heterocyclic(N within ring) dithiocarbamates) have been synthesized and successfully used as a solvent extractor. These compounds form complexes selectively as a neutral ligand with Ag(I), Hg(II) and Pd(II).

Keywords : xylylene bis(diisobutyl dithiocarbamate), neutral ligand, metal complex, Ag(I), Pd(II)

1. Introduction

Several references have been cited in the literature on the synthesis of macrocyclic polythiaethers[1] and dithiocarbamates[2] and remarkable ability to form complex with metal cations. The macrocyclic polythiaethers form complex as neutral ligand with five or six membered ring structure [3] and their ability to discriminate among closely related metal cations based on the relative fit of the ligand cavity size to metal ion radius[4]. While the dithiocarbamates form more stable four membered ring complex with metals as a nonselective ionic ligand[2,5]. Taking into account, it was felt necessary to investigate how far the substitution of xylylene as well as dialkyl and heterocyclic (N within ring) groups will affect the nature of the donor sulfur atom. It is expected that this noncyclic type compounds form complex as a neutral ligand with transition metals selectively due to flexible structure and appropriate position of two dithiocarbamate radicals. These compounds may also be useful as a solvent extractor and ion-sensor material for transition metal ions.

In this paper, we report the synthesis of some new compounds, o- and p-xylylene bis (diisopropyl, di-n-butyl, diisobutyl, N-metal-N-octadecyl, pyrrolidine and piperidine) dithiocarbamates.

2. Experimental

The structure of the synthesized compounds is shown in Fig. 1. All the compounds are prepared by the route as shown in scheme 1. The secondary amine 1 was firstly converted into respective dithiocarbamate 2 and finally bis-type compound 3 was obtained by the addition of o- or p-xylylene dibromide.

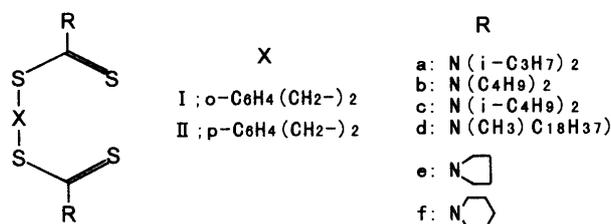
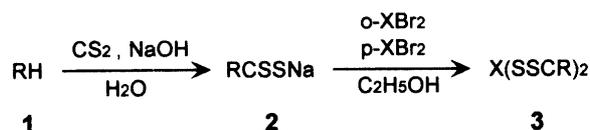


Fig. 1 Structure of synthesized compounds



Scheme 1

3. Results and Discussion

3-1 Synthesis of xylylene bis (dithiocarbamates)

The detailed procedure of o-xylylene bis (diisobutyl dithiocarbamate) is as follows:

The diisobutylamine (0.14 mol) was dissolved in water (300 ml) containing sodium hydroxide (0.14 mol) and isopropanol (25 ml) and dropwise carbon disulfide (0.14 mol) was added to the solution. The mixture was stirred for one hour to react at room temperature. The resultant precipitate of sodium N,

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*Department of Applied Chemistry and Chemical Engineering

**Kagoshima Prefectural Institute of Industrial Technology

Table 1. Characterization data of synthesized xylylene bis (dithiocarbamates)

Compound	Yield / %	Mp / °C	m / e (M ⁺)	IR / cm ⁻¹ ν C-S-C	NMR (in CDCl ₃)
Ia	26	109-110	456	720	1.43(d,24H), 4.63(s,4H), 7.30(m,4ArH)
IIa	37	140-143	456	730	1.45(d,24H), 4.50(s,4H), 7.23(m,4ArH)
Ib	69	55-56	512	740	0.9(t,12H), 1.33(m,8H), 1.7(m,8H), 3.6(t,4H), 3.92(t,4H), 4.59(s,4H), 7.3(m,4ArH)
IIb	65	111-113	512	730	0.9(t,12H), 1.33(m,8H), 1.7(m,8H), 3.6(t,4H), 3.92(t,4H), 4.49(s,4H), 7.28(m,4ArH)
Ic	47	88-90	512	720	0.89(d,24H), 2.28(m,4H), 3.56(d,8H), 4.47(s,4H), 7.08(m,4ArH)
IIc	52	120-121	512	730	0.98(d,24H), 2.37(m,4H), 3.80(d,8H), 4.61(s,4H), 7.45(m,4ArH)
Id	51	50-51	-	720	1.15(d,68H), 3.34(m,6H), 4.60(s,4H), 7.25(m,4ArH)
IIId	55	70-71	-	720	1.25(d,68H), 3.36(m,6H), 4.52(s,4H), 7.25(m,4ArH)
Ie	60	135-136	396	710	1.95(m,8H), 3.58(t,4H), 3.90(t,4H), 4.64(s,4H), 7.32(m,4ArH)
IIe	71	170-172	396	700	1.99(m,8H), 3.60(t,4H), 3.90(t,4H), 4.52(s,4H), 7.26(m,4ArH)
If	62	118-120	424	720	1.68(m,12H), 4.04(m,8H), 4.62(s,4H), 7.22(m,4ArH)
IIIf	24	191-193	424	700	1.71(m,12H), 4.02(m,8H), 4.52(s,4H), 7.31(m,4ArH)

N'-diisobutyl dithiocarbamate was filtered and crystallized with isopropanol, yield 27.4 g (87%), mp 99-100 °C. o-Xylylene bis (diisobutyl dithiocarbamate) was prepared by dissolving sodium N, N'-diisobutyl dithiocarbamate (0.1 mol) in ethanol (500 ml) and o-xylylene dibromide (0.05 mol) was added slowly to the solution under refluxing and stirring condition. After keeping the same condition for four hours the resultant precipitate was filtered, washed successively with water, dried and crystallized with ethanol to give white powdered, mp 88-90 °C. The characterization data of other members of the series, prepared similarly are given in Table 1.

3-2 Solvent extraction of metal ions

These compounds forms complex with Ag(I), Hg(II) and Pd(II) selectively. The selective complex formation ability of these compounds have been examined by solvent extraction. In all cases, the extraction conditions are kept constant.

The ligand (1 x 10⁻³ M) and metal ions (5 x 10⁻⁵ M) were dissolved in chloroform (20 ml) and water (20 ml) respectively. The perchlorate (1 x 10⁻² M) concentration was adjusted by using hydrogen perchlorate. The results of o- and p-xylylene bis (diisobutyl dithiocarbamate) (Ic and IIc) are summarized in Table 2. Extraction percentage of each metal cations can be mutually compared. These compounds form more stable complex with soft bases (class b) except Cd(II)

Table 2. Data for extractability (%) of various metals with Ic and IIc into chloroform

Metal ion	Na ⁺	K ⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Pd ²⁺	Ag ⁺	Cd ²⁺	In ³⁺	Sb ³⁺	Hg ²⁺	Pd ²⁺
Class of metal*	a	a	ab	ab	ab	ab	b	b	b	ab	ab	b	ab
Ic	0	0	0	0	5.7	2.2	100	96.1	0	0	4.4	88.8	3.0
IIc	0	0	0.6	0	1.3	4.7	100	67.1	0	0	3.5	20.8	2.6

*Classification of metals is based on HSAB sense[6].

than the soft acid (class a or ab).

This work demonstrates the synthesis of new o- and p-xylylene bis (dialkyl / heterocyclic (N within ring) dithiocarbamates) and usefulness of these compounds in solvent extraction due to selectively from complex with cations. The solvent extraction and ion-selective electrode results have been presented in our full manuscript.

References

1. a) D. St. C. Black and I. A. McLeon, *Tetrahedron Lett.*, **45**, 3961 (1969). b) W. Rosen and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4694 (1969). c) W. Rosen and D. H. Busch, *Inorg. Chem.*, **9**, 262 (1970). d) D. W. Allen, P. N. Braunton, I. T. Millar, and J. C. Tebby, *J. Chem. Soc. C*, 3454 (1971). e) L. A. Ochrymowycz, C. P. Mak, and J. D. Michna, *J. Org. Chem.*, **39**, 2079 (1974). f) D. Gerber, P. Chongsawangvirod, A. K. Leung, and L. A. Ochrymowycz, *J. Org. Chem.*, **42**, 2644 (1977).
2. G. D. Thorn and R. A. Ludwig, "The Dithiocarbamate and Related Compounds," Elsevier Publishing Co., Amsterdam-New York (1962).
3. a) K. Travis and D. H. Busch, *Inorg. Chem.*, **13**, 2591 (1974). b) P. H. Davis, L. K. White, and R. L. Belford, *Inorg. Chem.*, **14**, 1753 (1975). c) M. D. Glick, D. P. Gavel, L. L. Diaddario, and D. B. Rorabacher, *Inorg. Chem.*, **15**, 1190 (1976). d) R. E. Desimone and M. D. Glick, *J. Am. Chem. Soc.*, **98**, 762 (1976). e) S. G. Murry and F. R. Hartly, *Chem. Rev.*, **81**, 365 (1981). f) J. R. Hartman and S. R. Cooper, *J. Am. Chem. Soc.*, **108**, 1202 (1986). g) J. R. Hartman, E. J. Hinsta, and S. R. Cooper, *J. Am. Chem. Soc.*, **108**, 1208 (1986).
4. T. E. Jones, L. L. Zimmer, L. L. Diaddario, D. B. Rorabacher, and J. A. Ochrymowycz, *J. Am. Chem. Soc.*, **97**, 7163 (1975).
5. a) A. Hulanicki, *Talanta*, **14**, 1371 (1967). b) E. B. Sandell and H. Onishi, "Photometric Determination of Traces of Metals General Aspects," 4th ed. of Part I of Colorimetric Determination of Traces of Metals, John Wiley and Sons, Inc., New York (1978) pp. 512-532. c) D. Coucouranis, *Progr. Inorg. Chem.*, **11**, 233 (1970).
6. S. Ahrland, J. Chatt, and N. R. Davis, *Quart. Rev.*, London, **12**, 265 (1958).