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Thiadiphosphetane Disulfide as a Metal Extractant Which Shows High Ag+ Selectivity

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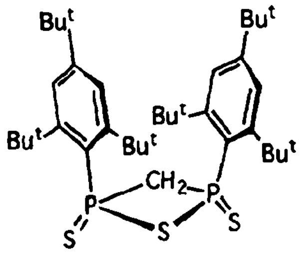
Abstracts: It was shown that *cis*-2,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,2,4-thiadiphosphetane 2,4-disulfide (**1**) acts as an excellent Ag^+-selective extractant. Two-phase solvent-extraction and spectral examination with ^1H and ^{31}P NMR established that **1** forms a 1:1 complex with Ag^+ using the P(=S)-S-P(=S) linkage designed in the rigid four-membered ring.

The metal recognition is achieved by a skillful combination of the "ion-size selectivity" with an ingenious selection of atoms and a spatial arrangement of those atoms. We recently synthesized *cis*-2,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,2,4-thiadiphosphetane 2,4-disulfide (**1**): the X-ray analysis disclosed that **1** has aromatic rings arranged like pincettes and an open space surrounded by three soft S atoms.[1] This structural characteristics strongly tempted us to apply **1** as a metal extractant, particularly that for soft metal ions. Examination with a two-phase solvent-extraction system has established that as expected, **1** shows the high affinity as well as the high selectivity toward Ag^+.[2,3]



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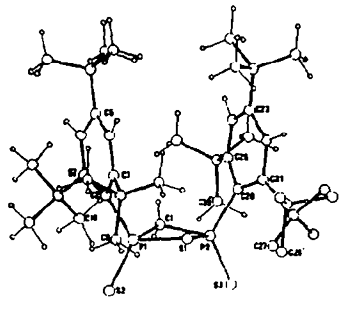

X-Ray structure of 1[1]

Two-phase solvent-extraction was carried out at 25 °C with an aqueous solution (25 ml, [metal salt] = 1.1×10^{-4} mol dm^{-3}, pH 5.3 with 0.1 mol dm^{-3} acetate buffer) and a chloroform solution (5 ml, [1] = 5.5×10^{-4} mol dm^{-3}). The mole ratio of the metal salt in the aqueous phase and 1 in the organic phase is 1:1. After shaking for 12 h, the concentration of metal salts in the aqueous phase was analyzed by atomic absorption spectroscopy. The extractability (Ex%) was defined as $[Ag^+]_{org} / [Ag^+]_{total}$. The results are summarized in Table 1. It is seen from Table 1 that **1** has the very high affinity for Ag^+ and the moderate affinity for Pd^{2+} and UO_2^{2+} whereas transition metal ions such as Cu^{2+}, Ni^{2+}, and Fe^{3+} were scarcely extracted. We surveyed the past literatures on the "metal preference" of analogous extractants. Dialkyl sulfides show the high affinity for Pd^{2+}.[4] "Hard" phosphorous oxides show the high affinity for "hard" UO_2^{2+}.[5] On the other hand, trialkylphosphine sulfides show the "metal preference" similar to **1** (*i.e.*, $Ag^+ > Pd^{2+} >$ transition metal ions).[6] The results manifest that in **1** the essential functional group used for metal-binding is the P=S group but not the -S- group. It is now clear that **1** acts as a useful Ag^+-selective extractant because of the P=S ····· Ag^+ interaction.

Table 1. Extraction of transition metal cation by **1**.

Metal Salt	Ex%
$Cu(NO_3)_2$	trace
$Ni(NO_3)_2$	trace
$Fe(NO_3)_3$	trace
$Fe(NO_3)_3$	42.1[b]
$AgNO_3$	86.6
$AgNO_3$	98.4[b]
$PdCl_2$	8.3
$PdCl_2$	14.2[b]
$K_4[UO_2(CO_3)_3]$	15.2[c]

[a] pH = 5.3 with 0.1 mol dm^{-3} acetate buffer.

[b] Toluene was used as an organic phase.

[c] pH = 5.9 with 0.01 mol dm^{-3} acetate buffer.

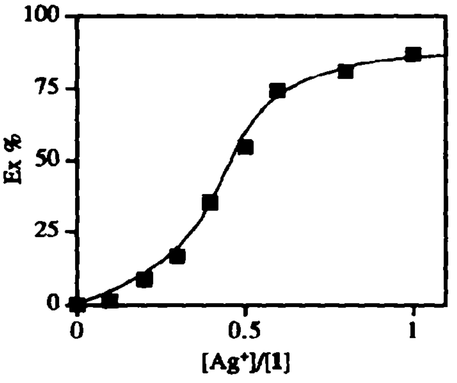

Fig. 1. Plot of Ex% *vs.* $[Ag^+] / [1]$ in two-phase solvent-extraction. **1** (5.5×10^{-4} mol dm^{-3}) was maintained constant.

Subsequently, we estimated Ag^+-extraction properties more in detail. Fig. 1 shows a plot of Ex% against $[Ag^+]$ / [**1**] (where [**1**] is maintained constant). The Ex% is almost saturated at $[Ag^+]$ / [**1**] = 1.0, indicating that the extracted species has 1:1 stoichiometry. However, the plot shows a sigmoidal curve but not a simple saturation curve. Probably, this peculiar dependence is caused by the aggregation of $AgClO_4$ in chloroform.

In ^{31}P NMR spectroscopy the δ_P (46.3 ppm in C_6D_6 at 25 °C in the absence of $AgClO_4$) shifted to lower magnetic field and was saturated at 62.2 ppm. Fig. 2 shows a plot of δ_P against $[Ag^+]$ / [**1**]: the shift saturation occurs at $[Ag^+]$ / [**1**] = 1.0 and the sigmoidal dependence is again observable at $[Ag^+]$ / [**1**] = 0 ~ 1.0 region. In ^1H NMR spectroscopy (in C_6D_6 at 25 °C) the PCH_2P methylene protons appear at 4.41 and 4.77 ppm. To assign the geminal protons we measured NOE with respect to the *tert*-Bu protons but failed because of the weak correlation. As shown in Fig. 3, the δ_H at higher magnetic field shifts to higher magnetic field while the δ_H at lower magnetic field shifts to lower magnetic field as the Ag^+ concentration increases. The breakpoints are again observed at $[Ag^+]$ / [**1**] = 1.0. According to the X-ray structure of **1**,[1] the distance between the two S atoms is 4.51 Å. Even though taking the van der Waals radius of S (1.80 Å), this distance is a little too long to tweeze Ag^+ (radius 1.15 Å) with the two S atoms. It is reasonable to consider, therefore, that upon the Ag^+ binding the two P=S groups are a little expanded and consequently the aromatic ring pincettes are closed. In this motion one of the two PCH_2P protons is shielded and the other deshielded.

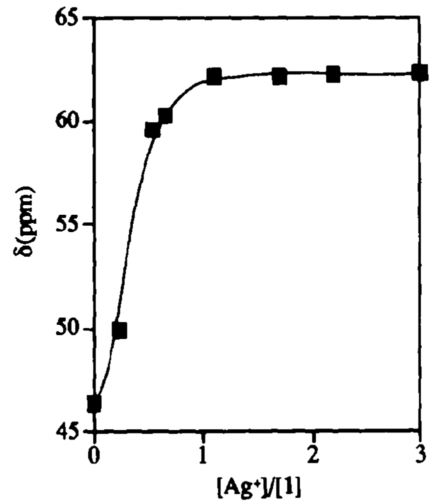

Fig. 2. Plot of δ_P *vs.* $[Ag^+]$ / [**1**] in C_6D_6 at 25 °C.

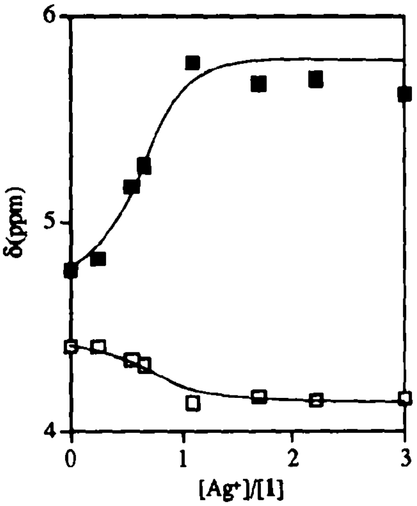

Fig. 3. Plots of δ_H for the two PCH_2P methylene protons *vs.* $[Ag^+]$ / [**1**] in C_6D_6 at 25 °C.

In conclusion, the present paper reveals that the P(=S)-S-P(=S) linkage designed in a rigid four-membered ring serves as an excellent Ag^+-selective extractant forming a 1:1 complex. This is a new and unique entry for the Ag^+-selective metal receptor.

References

1. Toyota, K.; Yoshifuji, M.; Hirotsu, K. *Chem. Lett.*, **1990**, 643.
2. For extraction of heavy metal ions with "soft"-atom-containing extractants see Beamish, F. E.; *Talanta*, **14**, *991*, 1967; Mojski, M. *Chemia Analityczna*, **24**, *207*, 1979; Gindin, L. M. *Ion Exchange and Solvent Extraction*; Marinsky, J. A.; Marcus, Y., Eds.; Marcel Dekker: New York, 1981, Vol. 8, p. 311.
3. For Ag^+-selective extractants see Blake, A. J.; Reid, G.; Schröder, M. *J. Chem. Soc., Chem. Commun.*, **1992**, 1074; Clarkson, J.; Yagbasan, R.; Blower, P. J.; Rawle, S. C.; Cooper, S. R. *ibid.*, **1987**, 950; Sato, M.; Kubo, M.; Ebine, S.; Akabori, S. *Bull. Chem. Soc. Jpn.*, **57**, *421*, 1984, and references cited therein. They are thiacrown ether derivatives.
4. Nikolaev, A. V.; Torgov, V. G.; Mikhailov, V. A.; Andrievski, V. N.; Bakovets, K. A.; Bondarenko, M. F.; Gil'bert, E. N.; Kotlyarevskii, I. L.; Mardezova, G. N.; Shatskaya, S. S. *Izv. Sib. Otd. Akad. Nauk SSSR. Ser. Khim. Nauk*, **9**, *54*, 1970.
5. Pozas-Tormo, R.; Moreno-real, L.; Martinez-Lara, M.; Bruque-Gamez, S. *Inorg. Chem.*, **26**, *1442*, 1987; Cromer, D. T.; Ryan, R. R.; Karthikegar, S.; Paine, R. T. *Inorg. Chim. Acta*, **172**, *165*, 1990.
6. Hitchcock, R. B.; Dean, J. A.; Handley, H. *Anal. Chem.*, **35**, *254*, 1963.

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