

Note

Paper chromatographic studies of metal complexes

II. Comparison of square planar and octahedral complexes

R. K. RAY*

Department of Chemistry, Rama Krishna Mission Vivekananda Centenary College, Rahara-743186, 24-Parganas (North), West Bengal (India)

and

GEORGE B. KAUFFMAN

Department of Chemistry, California State University, Fresno, Fresno, CA 93740 (U.S.A.)

(First received May 24th, 1989; revised manuscript received December 7th, 1989)

Despite numerous theories (adsorption, partition, solvent extraction, ion exchange, etc.), the actual mechanism of the chromatographic separation of inorganic compounds on filter paper is not well understood¹⁻¹². It may be considered as consisting of the following steps: (1) adsorption of metal ions by the cellulose molecules of filter paper¹³⁻¹⁵ (Fig. 1a); (2) desorption of metal ions by acids adsorbed as a result of the formation of oxonium ions by the interaction of cellulose with the H⁺ ions of an acid^{14,16,17} (Fig. 1b); and (3) solvation of the desorbed ions by solvent^{18,19} and the washing away of the solvated complex by the solvent stream.

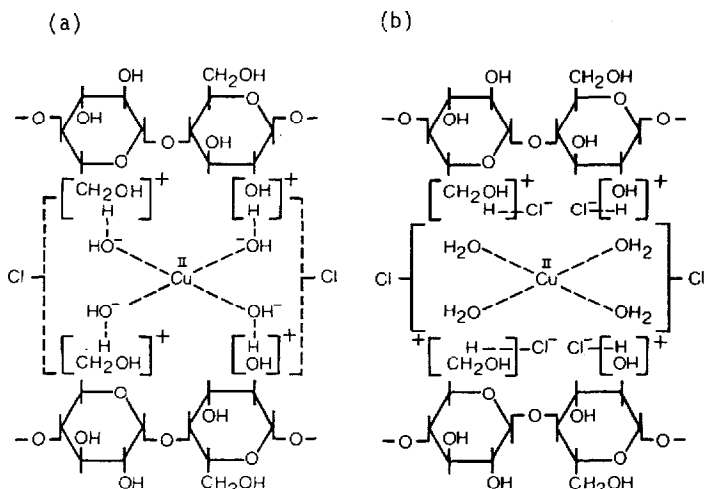


Fig. 1. (a) Mode of adsorption of Cu²⁺ aqua complex on cellulose. (b) Mode of desorption of Cu²⁺ aqua complex on cellulose in the presence of H⁺ ions.

In this paper, the movement of square planar metal(II) complexes on cellulose is compared, under identical conditions, with that of octahedral metal(III) and metal(II) complexes.

EXPERIMENTAL

Materials

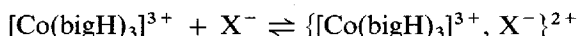
The complex compounds were synthesized according to published procedures²⁰⁻²⁶. Their purity was confirmed by elemental analysis and spectral measurements. The complexes are very stable at pH \approx 7, but they begin to dissociate at pH $<$ 7²⁷.

Procedure

The complex compounds were dissolved in water and subjected to ascending chromatography using Whatman No. 1 paper strips (3 cm \times 52 cm). Aqueous solutions (0.1 M) of various salts were used as developers (Table II). The chromatograms were developed for about 3 h at 25°C. The cobalt(III) complexes were detected by spraying with an aqueous solution of sodium sulfide, which colors the spots black. With nickel(II) and copper(II) complexes an ethanolic solution of dithiooxamide (rubeanic acid) gave blue and green spots, and with palladium(II) complexes an acidic solution of dithiooxamide gave yellow spots.

RESULTS AND DISCUSSION

When cobalt(III) complexes of different charges were developed with water, only anionic and neutral complexes easily migrated on paper and yielded high R_F values (*ca.* 0.9). However, the cationic complexes remained at the baseline or diffused a long distance from the point of application²⁷. The paper (cellulose) is charged negatively in contact with water, and the cellulose anion strongly attracts the cationic complexes²⁷. Such strong binding was reduced considerably by using ionic electrolytes²⁷. In general, the R_F values of cationic complexes belonging to a particular charge type (+3, +2 or +1) are the lowest in KI solution, and then gradually increase as the electrolyte changes to KBr, KCl, etc., and then to bi-univalent electrolytes such as K₂SO₄, Na₂S₂O₃, etc. These variations in R_F values indicate outer-sphere association between the complex cations and the anion present in the developer²⁷. Investigations of the outer-sphere association constants of [Co(NH₃)₆]³⁺, [Co(bigH)₃]³⁺, etc., have shown that these constants follow the order^{28,29} I⁻ $<$ Br⁻ $<$ Cl⁻ \ll SO₄²⁻. The larger the association constants, the larger will be the R_F values. The anion of the developer reduces the overall charge of the complex cation and thus allows easy passage of the complex ion along the anionic filter-paper:



(X⁻ = Cl⁻, Br⁻ or I⁻);

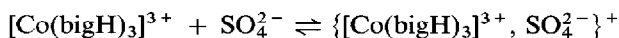


TABLE I

R_F VALUES FOR OCTAHEDRAL Co(III) AND Ni(II) COMPLEXES WITH DIFFERENT DEVELOPERS (0.1 M)

Complex ^a	KI	KBr	KCl	CH ₃ COONH ₄	K ₂ SO ₄	Na ₂ S ₂ O ₃	KNaC ₄ H ₄ O ₆
[Co(bigH) ₃]Cl ₃	0.50	0.54	0.60	0.48	0.82	0.85	0.84
[Co(MebigH) ₃]Cl ₃	0.52	0.57	0.62	0.49	0.83	0.87	0.90
[Co(NH ₃) ₆]Cl ₃	0.40	0.55	0.65	0.40	0.85	0.87	0.90
[Co(PhbigH) ₃]Cl ₃	0.45	0.52	0.59	0.46	0.90	0.90	0.84
[Co(gly)(bigH) ₂]Cl ₂	0.65	0.67	0.70	0.64	0.93	0.91	0.93
[Co(α-alan)(bigH) ₂]I ₂	0.67	0.71	0.78	0.67	0.96	0.95	0.96
[Co(β-alan)(bigH) ₂]I ₂	0.62	0.65	0.73	0.63	0.91	0.92	0.94
[Co(IDA)(bigH) ₂]Cl	0.77	0.81	0.82	0.78	0.95	0.93	0.94
[Co(en) ₂ CO ₃]Cl	0.78	0.79	0.83	0.79	0.94	0.94	0.95
[Co(NH ₃) ₃ (NO ₂) ₃]	0.95	0.93	0.96	0.93	1.00	1.00	1.00
[Co(gly) ₃]	0.96	0.94	0.96	0.95	1.00	1.00	1.00
[Ni(en) ₃]Cl ₂	0.43	0.46	0.52	0.94	0.73	0.72	0.73
[Ni(gly) ₂ (H ₂ O) ₂]	0.94	0.94	0.96	0.96	0.98	0.99	0.99
[Co(dipy)(bigH) ₂]Cl ₃	0.52	0.55	0.61	0.53	0.83	0.84	0.84
[Co(<i>o</i> -phen)(bigH) ₂]Cl ₃	0.49	0.53	0.61	0.50	0.86	0.85	0.85
K[Co(NO ₂) ₂ (gly) ₂]	1.00	1.00	1.00	1.00	1.00	1.00	1.00
NH ₄ [Co(NO ₂) ₄ (NH ₃) ₂]	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Na ₃ [Co(NO ₂) ₆]	1.00	1.00	1.00	1.00	1.00	1.00	1.00
K ₃ [Co(NO ₂) ₆]	1.00	1.00	1.00	1.00	1.00	1.00	1.00

^a alanH = Alanine; bigH = biguanide; dipy = α,α'-dipyridyl; en = ethylenediamine; glyH = glycine; IDAH₂ = iminodiacetic acid; MebigH = N¹-methylbiguanide; *o*-phen = *o*-phenanthroline; PhbigH = N¹-phenylbiguanide.

Square planar complexes of nickel(II), copper(II) and palladium(II) behaved identically when water, methylamine, ethylamine, pyridine, etc., were used as developing solvents. In order to reduce such strong binding of the cationic complexes, several electrolytes were used (Table I). With water-containing KCl (or KBr or KI) developer, although the complexes moved from the point of application, the complexes soon diffused a long distance along the filter-paper. Other aqueous salt solutions were also used as developers.

However, KCl-containing pyridine developer not only helped the spot to migrate from the point of application but also provided a good-sized spot of about 1.5 cm (Table II). Pyridine substantially increased the solubility of the complexes. The solubilities of [Cu(bigH)₂]Cl₂, [Cu(MebigH)₂]Cl₂, [Cu(EtbigH)₂]Cl₂ and [Cu(PhbigH)₂]Cl₂ are 18.92, 7.15, 0.38 and 0.40 g per 100 ml, respectively, in 0.5 M KCl and 20.84, 7.96, 0.45 and 0.48 g per 100 ml in 0.5 M KCl-pyridine (100:5, v/v) developing solvent.

Table II shows that an increase in the molecular weight of the alkyl group substituted on the N¹ atom of the biguanide molecule increases the R_F values of the corresponding copper(II), nickel(II) and palladium(II) bis(biguanide) complexes. However, phenyl substitution lowers the R_F values (Table II). Because biguanide, alkybiguanides and arylbiguanides have more or less similar basic characters (pK_1 and pK_2 of bigH = 11.5, 2.9; MebigH = 11.4, 3.0; EtbigH = 11.5, 3.1; and PhbigH = 10.7, 2.2), the attractive influence of the doubly charged cations on the cellulose anion

TABLE II

 R_F VALUES OF SQUARE PLANAR METAL(II) COMPLEXES WITH DIFFERENT DEVELOPERS

Complex ^a	Developer I ^b	Developer II ^c	Developer III ^d
[M(bigH) ₂]Cl ₂	0.48	0.75	0.42
[M(MebigH) ₂]Cl ₂	0.54	0.81	0.53
[M(EtbigH) ₂]Cl ₂	0.65	0.85	0.60
[M(Pr ⁱ bigH) ₂]Cl ₂	0.70	0.91	—
[M(PhbigH) ₂]Cl ₂	0.43	0.70	0.31

^a bigH = Biguanide; EtbigH = N¹-ethylbiguanide; MebigH = N¹-methylbiguanide; PhbigH = N¹-phenylbiguanide; PrⁱbigH = N¹-isopropylbiguanide.

^b 100 ml 0.5 M KCl + 5 ml pyridine; M = Cu(II).

^c 100 ml 1 M KCl + 5 ml pyridine; M = Ni(II).

^d 70 ml 0.5 M KCl + 30 ml pyridine-water (50:50), M = Pd(II).

is also probably similar. However, replacement of the H atom attached to the N¹ atom of the biguanide molecule by hydrophobic groups should reduce considerably the chances of forming hydrogen-bonded species with cellulose anions, and thus increasing substitution should result in higher R_F values.

If solubility alone were responsible for differences in the R_F values, a reverse order with increasing alkyl substitution should be observed. The increase in R_F values from biguanide to higher alkyl-substituted biguanides is also likely to be related to the inductive influence of the electron-releasing alkyl groups, which diminishes the overall charge on the complex cation to some extent. This lowering of charge should increase the R_F values, whereas electron-withdrawing phenyl substitution should lead to lower R_F values.

Ammonium acetate solution of pH *ca.* 6.5 was not a good developer as spectrophotometric studies revealed that for all these square planar complexes the electronic spectra were substantially modified. This developer, therefore, does not provide R_F values of genuine metal(II) bis(biguanide) complexes.

It is noteworthy that nickel(II) complexes are likely to form the very insoluble [Ni(bigH)₂]SO₄ in aqueous K₂SO₄ developer²⁰. By virtue of its extreme insolubility, the spot remained on the baseline. Similarly, Na₂S₂O₃ solution was unsuitable, particularly for copper(II) complexes, because in the presence of Na₂S₂O₃, copper(II) species may be reduced to copper(I) species. Therefore, if the overall charge of the complex cation alone were responsible for the retention of complex cations, migration of square planar complex cations on paper would have been equally possible by using only a suitable electrolyte developer. Therefore, it can be safely assumed that the retention of square planar complexes on a cellulose bed is due to direct coordination of the cellulose anion in the metal(II) complex, making the complex a hexacoordinate structure. It could be noted that in the presence of suitable coordinating ligands a square planar complex of palladium(II) or platinum(II) may add two more ligands and be transformed into an octahedral complex ($D_{4h} \rightarrow O_h$ symmetry)³⁰.

During thin-layer chromatographic studies, Baba and Yoneda³¹ observed that tris(glycinato)cobalt(III) (O_h symmetry) moved almost with the solvent front, whereas bis(glycinato)copper(II), also a non-electrolyte, remained at the baseline. Such

a strong retention of bis(glycinato)copper(II) on silica gel is due to direct coordination of silica to the copper(II) complex, giving it a hexacoordinate structure ($D_{4h} \rightarrow O_h$ symmetry)³¹. It should be noted that bis(glycinato)copper(II) crystallizes as a monohydrate, and its X-ray pattern shows a distorted octahedral structure through coordination of a water molecule along a carboxyl oxygen of the neighboring molecule³².

ACKNOWLEDGEMENTS

R.K.R. thanks Prof. R. L. Dutta, Department of Chemistry, University of Burdwan, and Prof. N. Saha, University College of Science, Calcutta, for providing some facilities and for helpful discussions. The authors are grateful to the referees for valuable suggestions for improving the paper.

REFERENCES

- 1 C. S. Hanes and F. A. Isherwood, *Nature (London)*, 164 (1949) 1107.
- 2 D. P. Burma, *Anal. Chem.*, 25 (1953) 549.
- 3 T. Schonfeld and E. Broda, *Mikrochemie Ver. Mikrochim. Acta*, 36/37 (1951) 537.
- 4 J. B. Schuttc, *Nature (London)*, 171 (1953) 839.
- 5 R. Consden, A. H. Gordon, A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, 38 (1944) 224.
- 6 A. J. P. Martin, *Annu. Rev. Biochem.*, 19 (1950) 517.
- 7 M. Lederer, *Anal. Chim. Acta*, 5 (1951) 185.
- 8 A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, 35 (1941) 358.
- 9 F. H. Pollard and J. F. W. McOmie, *Chromatographic Methods of Inorganic Analysis*, Academic Press, New York, 1953.
- 10 I. M. Hais and K. Macek, *Paper Chromatography; a Comprehensive Treatise*, Academic Press, New York, 1963.
- 11 R. Stock and C. B. F. Rice, *Chromatographic Methods*, Chapman & Hall, London, 2nd ed., 1968.
- 12 M. Lederer (Editor), *Chromatogr. Rev.*, 1 (1959), 2 (1960), 3 (1961).
- 13 T. J. Beckmann and M. Lederer, *J. Chromatogr.*, 3 (1960) 493.
- 14 M. Lederer, *J. Chromatogr.*, 6 (1961) 437, 518.
- 15 K. A. Kraus, D. C. Michelson and F. Nelson, *J. Am. Chem. Soc.*, 81 (1959) 3204.
- 16 L. Ossicini and M. Lederer, *J. Chromatogr.*, 17 (1965) 387.
- 17 H. M. Irving, *Q. Rev. Chem. Soc.*, 5 (1951) 200.
- 18 W. C. Brown, *Nature (London)*, 143 (1939) 377.
- 19 R. L. Dutta, R. K. Ray and G. B. Kauffman, *Coord. Chem. Rev.*, 28 (1979) 23.
- 20 P. Rây, *Chem. Rev.*, 61 (1961) 313.
- 21 A. Syamal, *J. Sci. Ind. Res.*, 37 (1978) 661.
- 22 W. G. Palmer, *Experimental Inorganic Chemistry*, Cambridge University Press, Cambridge, 1959, pp. 530, 539 and 548.
- 23 J. B. Work, *Inorg. Synth.*, 2 (1946) 221.
- 24 R. L. Dutta and S. Sarkar, *J. Indian Chem. Soc.*, 44 (1967) 832.
- 25 R. L. Dutta and A. Bhattacharya, *J. Indian Chem. Soc.*, 52 (1975) 1002.
- 26 R. L. Dutta, S. Sarkar and K. K. Bhattacharya, *J. Indian Chem. Soc.*, 50 (1973) 235.
- 27 R. K. Ray and G. B. Kauffman, *J. Chromatogr.*, 442 (1988) 381.
- 28 M. K. De and R. L. Dutta, *J. Indian Chem. Soc.*, 52 (1975) 67.
- 29 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, Wiley, New York, 2nd ed., 1967, p. 37.
- 30 D. Banerjee, F. Basolo and R. G. Pearson, *J. Am. Chem. Soc.*, 79 (1957) 4055.
- 31 T. Baba and H. Yoneda, *Bull. Chem. Soc. Jpn.*, 43 (1970) 2478.
- 32 K. Nakamoto and P. J. McCarthy, *Spectroscopy and Structure of Metal Chelate Compounds*, Wiley, New York, 1968, p. 40.