



e-ISSN: 2319-8753 | p-ISSN: 2347-6710

IJIRSET

International Journal of Innovative Research in
SCIENCE | ENGINEERING | TECHNOLOGY



INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

Volume 11, Issue 11, November 2022

ISSN INTERNATIONAL
STANDARD
SERIAL
NUMBER
INDIA

Impact Factor: 8.118

 9940 572 462

 6381 907 438

 ijirset@gmail.com

 www.ijirset.com



Extraction of Some Transition Metal Complexes

Dr. Yogesh Chahar

Associate Professor, Dept. of Chemistry, S.B.D. Govt. College, Sardarshahar, Churu, Rajasthan, India

ABSTRACT: In chemistry, a **transition metal** (or **transition element**) is a chemical element that has a partly filled d subshell in elemental form or as an ion in compounds, which allows the d orbitals to participate in chemical bonding. The transition metals are approximately those elements in the d-block of the periodic table, a criterion that is sometimes used to define them. Definitions of the term transition metal vary, but usually include all the elements of groups 4 through 11, and the group 3 elements scandium and yttrium. They often also include lanthanum and actinium, or lutetium and lawrencium. The f-block lanthanide and actinide series are called **inner transition metals** and are sometimes considered to be transition metals.

Since they are metals, they are lustrous and have good electrical and thermal conductivity. Most (with the exception of group 11 and group 12) are hard and strong, and have high melting and boiling temperatures. They form compounds in any of two or more different oxidation states and bind to a variety of ligands to form coordination complexes that are often coloured. They form many useful alloys and are often employed as catalysts in elemental form or in compounds such as coordination complexes and oxides. Most are strongly paramagnetic because of their unpaired d electrons, as are many of their compounds. All of the elements that are ferromagnetic near room temperature are transition metals (iron, cobalt and nickel) or inner transition metals (gadolinium).

KEYWORDS: transition, complexes, metal, extraction, chemical, catalysts, temperature, compounds

I. INTRODUCTION

Recent studies on complex formation have revealed that the ligand structure plays a critical role in selectivity for metal ions. In previous reports, 1-3 it has been shown that poly(pyrazolyl)borates, of which the basic structure is $[\text{HnB}(\text{pz})_4 - \text{n}]^-$ ($\text{n} = 0-2$), have a unique selectivity for metal ions due to different steric factors from the conventional ligands. The selectivity of tripodal tridentate ligands, $[\text{HB}(\text{pz})_3]^-$, $[\text{B}(\text{pz})_4]^-$ and $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]^-$, for group 2 metal ions was studied by solvent extraction. $[\text{HB}(\text{pz})_3]^-$ extracted Mg^{2+} and Ca^{2+} effectively and Sr^{2+} to some extent. However, $[\text{B}(\text{pz})_4]^-$ extracted Mg^{2+} but not Ca^{2+} , because it is hard for $[\text{B}(\text{pz})_4]^-$ to increase the bite size due to intraligand contact between pyrazolyl rings and $[\text{B}(\text{pz})_4]_2\text{Ca}$ was not stable enough to be extracted. Moreover, $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]^-$ is selective for Ca^{2+} over Mg^{2+} and has improved extractability for Sr^{2+} and Ba^{2+} , because methyl groups on the 3-position of the pyrazolyl ring hinder A_2M complex formation for small metal ions through interligand contact, while they stabilize the complex of large metal ions through the shielding effect. Here we report the results on solvent extraction of Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} with poly(pyrazolyl)borates. To explore the origin of the selectivity, X-ray crystal structures of the extracted species have been determined for $[\text{HB}(\text{pz})_3]^-$, $[\text{B}(\text{pz})_4]^-$, $[\text{HB}(3\text{-Mepz})_3]^-$ and $[\text{B}(3\text{-Mepz})_4]^-$. The X-ray structures are compared precisely and steric factors controlling the selectivity are discussed.

Reagents and apparatus

$\text{K}[\text{HB}(\text{pz})_3]$, $\text{K}[\text{B}(\text{pz})_4]$, $\text{K}[\text{HB}(3\text{-Mepz})_3]$, $\text{K}[\text{B}(3\text{-Mepz})_4]$, $\text{K}[\text{HB}(3\text{-iPrpz})_3]$ and $\text{K}[\text{B}(3\text{-iPrpz})_4]$ were synthesized as previously reported. All other chemicals were reagent-grade and distilled water was used throughout. Metal ion and boron concentrations were determined with a PERKIN ELMER OPTIMA 3300-XL inductively coupled plasma emission spectrometer or a HITACHI Z-8100 polarized Zeeman atomic absorption spectrophotometer.

Distribution of poly(pyrazolyl)borates

Acid dissociation and partition constants of $[\text{HB}(\text{pz})_3]^-$, $[\text{B}(\text{pz})_4]^-$, $[\text{HB}(3\text{-Mepz})_3]^-$ and $[\text{B}(3\text{-Mepz})_4]^-$ were studied by solvent extraction in a similar manner to reported previously.^{3,7}



Extraction of first-series transition metal and Cd²⁺ ions

An aliquot of chloroform (10 mL) was shaken with the equal volume of an aqueous phase containing 10⁻² M of ligand and metal ion (10⁻⁴ M) at 25 ± 1 °C. The pH of the aqueous phase was adjusted with hydrochloric acid, acetic acid and appropriate Goods' buffer to study the effect of pH on the extraction percentage (%E). The metal concentration in the aqueous phase was determined using Z-8100 or OPTIMA 3300-XL. The metal concentration in the organic phase was measured after backextraction into 6 M hydrochloric acid or nitric acid. For [HB(pz)3] - and [B(pz)4] - , the extraction constant (K_{ex}) was determined in the aqueous phase where the sum of the concentrations of hydrochloric acid and lithium chloride was 1.5 M, and the concentrations were 10⁻³ M for the ligands and 10⁻⁵ M for the metal ions. For [HB(3-iPrpz)3] - and [B(3-iPrpz)4] - , the ligand was dissolved in chloroform. The concentration of ligand was 10⁻³ M and that of metal ion in the aqueous was 10⁻⁵ M.

Preparation of [HB(pz)3] - [B(pz)4] - , [HB(3-Mepz)3] - and [B(3-Mepz)4] – complexes

Eighty milliliters of 0.05 M sodium hydroxide containing ligand (6.0 mmol) was added to 1.0 M hydrochloric acid (10 mL) containing metal salt (3.0 mmol). Sodium hydroxide (1.0 M) was added and mixed until a precipitate no longer formed. After 20 min, the precipitate was filtered off and washed with distilled water and methanol. Crystals for the analytical sample and the X-ray structure were obtained by recrystallization from chloroform, dichloromethane, diethyl ether or acetonitrile.

X-ray structure determination

Crystals were mounted onto fine glass fibers with epoxy cement. The lattice parameters and intensity data were measured on a Rigaku AFC7R four-circle diffractometer with Ni-filtered Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) at 20 ± 1 °C. An ω -2 θ scan to a maximum 2 θ values of 120-140° was used. An empirical absorption correction using the program DIFABS 8 or that based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structures were solved by direct methods 9-11 and expanded using Fourier technique.¹² The non-hydrogen atoms were refined anisotropically. Hydrogens were fixed at the positions generated by calculation. All calculations were performed using the teXsan crystallographic software package developed by Molecular Structure Corporation

Structure of poly(pyrazolyl)borate complexes

For all the studied complexes (Table 3) except [B(pz)4]2Mn, [HB(3-Mepz)3]2Ni and [B(3-Mepz)4] - complexes, there are two crystallographically independent molecules within a unit cell. These two molecules resemble each other. The molecule is monomeric with no short intermolecular contacts. Each ligand is coordinated to the metal atom in a tridentate fashion, and the geometry about the metal atom is a trigonally distorted octahedron. For [B(pz)4] - and [B(3-Mepz)4] - complexes, the noncoordinated pyrazolyl rings stand out in the direction opposite the metal atom.

II. DISCUSSION

The terms transition metal (or transition element) are defined in several different ways:

- The IUPAC definition^[4] defines a transition metal as "an element whose atom has a partially filled d sub-shell, or which can give rise to cations with an incomplete d sub-shell".
- Many scientists describe a "transition metal" as any element in the d-block of the periodic table, which includes groups 3 to 12 on the periodic table.^{[5][6]} In actual practice, the f-block lanthanide and actinide series are also considered transition metals and are called "inner transition metals".
- Cotton and Wilkinson^[7] expand the brief IUPAC definition (see above) by specifying which elements are included. As well as the elements of groups 4 to 11, they add scandium and yttrium in group 3, which have a partially filled d subshell in the metallic state. Lanthanum and actinium, which they consider group 3 elements, are however classified as lanthanides and actinides respectively.

In the d-block, the atoms of the elements have between zero and ten d electrons.



Transition metals in the d-block										
Group	3	4	5	6	7	8	9	10	11	12
Period 4	₂₁ Sc	₂₂ Ti	₂₃ V	₂₄ Cr	₂₅ Mn	₂₆ Fe	₂₇ Co	₂₈ Ni	₂₉ Cu	₃₀ Zn
5	₃₉ Y	₄₀ Zr	₄₁ Nb	₄₂ Mo	₄₃ Tc	₄₄ Ru	₄₅ Rh	₄₆ Pd	₄₇ Ag	₄₈ Cd
6	₇₁ Lu	₇₂ Hf	₇₃ Ta	₇₄ W	₇₅ Re	₇₆ Os	₇₇ Ir	₇₈ Pt	₇₉ Au	₈₀ Hg
7	₁₀₃ Lr	₁₀₄ Rf	₁₀₅ Db	₁₀₆ Sg	₁₀₇ Bh	₁₀₈ Hs	₁₀₉ Mt	₁₁₀ Ds	₁₁₁ Rg	₁₁₂ Cn

Relationship to f-block elements

The elements of groups 4–11 are generally recognized as transition metals, justified by their typical chemistry, i.e. a large range of complex ions in various oxidation states, coloured complexes, and catalytic properties either as the element or as ions (or both). Sc and Y in group 3 are also generally recognized as transition metals. However, the elements La–Lu and Ac–Lr and group 12 attract different definitions from different authors.

1. Many chemistry textbooks and printed periodic tables classify La and Ac as group 3 elements and transition metals, since their atomic ground-state configurations are s^2d^1 like Sc and Y. The elements Ce–Lu are considered as the "lanthanide" series (or "lanthanoid" according to IUPAC) and Th–Lr as the "actinide" series.^{[8][9]} The two series together are classified as f-block elements, or (in older sources) as "inner transition elements". However, this results in a split of the d-block into two quite uneven portions.^[10]
2. Some inorganic chemistry textbooks include La with the lanthanides and Ac with the actinides.^{[7][11][12]} This classification is based on similarities in chemical behaviour (though this similarity mostly only exists among the lanthanides) and defines 15 elements in each of the two series, even though they correspond to the filling of an f subshell, which can only contain 14 electrons.^[13]
3. A third classification defines the f-block elements as La–Yb and Ac–No, while placing Lu and Lr in group 3.^[14] This is based on the Aufbau principle (or Madelung rule) for filling electron subshells, in which 4f is filled before 5d (and 5f before 6d), so that the f subshell is actually full at Yb (and No), while Lu has an $[]s^2f^{14}d^1$ configuration. (Lr is an exception where the d electron is replaced by a p electron, but the energy difference is small enough that in a chemical environment it often displays d-occupancy anyway.) La and Ac are, in this view, simply considered exceptions to the Aufbau principle with electron configuration $[]s^2d^1$ (not $[]s^2f^1$ as the Aufbau principle predicts).^[15] Excited states for the free atom and ion can become the ground state in chemical environments, which justifies this interpretation; La and Ac have vacant low-lying f subshells which are filled in Lu and Lr, so excitation to f orbitals is possible in La and Ac but not in Lu or Lr. This justifies the idea that La and Ac simply have irregular configurations (similar to Th as s^2d^2), and that they are the real beginning of the f-block.^[16]

As the third form is the only form that allows simultaneous (1) preservation of the sequence of increasing atomic numbers, (2) a 14-element-wide f-block, and (3) avoidance of the split in the d-block, it has been suggested by a 2021 IUPAC preliminary report as the preferred form.^[13] Such a modification, treating Lu as a transition element rather than as an inner transition element, was first suggested by Soviet physicists Lev Landau and Evgeny Lifshitz in 1948. Following this, it was then suggested by many other physicists and chemists, and was generally the classification adopted by those who considered the issue, but textbooks generally lagged in adopting it.



Sterically efficient structure of [HB(pz)3] –

[HB(pz)3] - can adopt a conformation suitable for tridentate coordination without severe intraligand contact. Further, the mutually staggered conformation prevents the interligand contact, favoring formation of the six-coordinate A2M complex. The increase in steric hindrance accompanying the A2M complex formation should be fairly small. That is, [HB(pz)3] - is sterically efficient in occupying a six-coordination.

Intraligand contact by noncoordinated pyrazolyl ring in [B(pz)4] –

When [B(pz)4] - widens the bite size (the distance between the donor nitrogen atoms) so as to coordinate large metal ions, such as Mn²⁺ and Cd²⁺, the steric repulsion between the coordinated and noncoordinated pyrazolyl rings is enhanced. It is most likely that the strain energy accompanying complexation becomes large and the stability constant is decreased more for the large metal ions. Consequently, [B(pz)4] - extracts Mn²⁺ and Cd²⁺ at higher pH than [HB(pz)3] –

The interligand contact between 3-methyl groups can occur and hinder complex formation. Since the Me...Me distance is shorter for [B(3-Mepz)4] - complexes, the interligand contact is severer for them. Therefore, the substituents of 3-position of pyrazolyl rings decrease the stability of the complexes of small metal ions. The extracted species of [HB(3-iPrpz)3] - complexes had not been determined so far. The extracted species of Cu²⁺ and Zn²⁺ with [B(3-iPrpz)4] - are A2M on the basis of the slope analysis. Trofimenko et al. 6 have obtained the precipitation of [B(3-iPrpz)4]2Co and determined the X-ray structure (Fig. 5). Each ligand is coordinated to the cobalt atom in a bidentate fashion. The noncoordinated ring farthest from the metal is oriented so as to bisect the planes of the two coordinated rings. The fourth ring is oriented perpendicular to the distant noncoordinated ring. The four isopropyl groups are arrayed around the equator of metal. Thus, [B(3-iPrpz)4] - is not suitable for tridentate coordination to Co²⁺. Under our experimental conditions, [B(3-iPrpz)4]2Co is not extracted. It seems that [B(3-iPrpz)4] 2Co is not stable enough to be extracted into the chloroform compared with [B(3-iPrpz)4]2Cu and [B(3-iPrpz)4]2Zn. The structure of [B(3-iPrpz)4]2Cu and [B(3-iPrpz)4]2Zn are not known yet.

III. RESULTS

The general electronic configuration of the d-block elements is [noble gas](n – 1)d¹⁻¹⁰ns⁰⁻². Here "[noble gas]" is the configuration of the last noble gas preceding the atom in question, and n is the highest principal quantum number of an occupied orbital in that atom. For example Ti (Z = 22) is in period 4 so that n = 4, the first 18 electrons have the same configuration of Ar at the end of period 3, and the overall configuration is [Ar]3d²4s². The period 6 and 7 transition metals also add core (n – 2)f¹⁻¹⁴ electrons, which are omitted from the tables below. The single exception is lawrencium, which has a 7p occupancy due to relativistic effects that become important at such high Z (though the p orbitals can also contribute to chemical bonding in lighter transition elements).

The Madelung rule predicts that the inner d orbital is filled after the valence-shell s orbital. The typical electronic structure of transition metal atoms is then written as [noble gas]ns²(n – 1)d^m. This rule is however only approximate – it only holds for some of the transition elements, and only then in the neutral ground states.

The d subshell is the next-to-last subshell and is denoted as (n – 1)d subshell. The number of s electrons in the outermost s subshell is generally one or two except palladium (Pd), with no electron in that s sub shell in its ground state. The s subshell in the valence shell is represented as the ns subshell, e.g. 4s. In the periodic table, the transition metals are present in eight groups (4 to 11), with some authors including some elements in groups 3 or 12.

The elements in group 3 have an ns²(n – 1)d¹ configuration, except for lawrencium (Lr): its 7s²7p¹ configuration exceptionally does not fill the 6d orbitals at all. The first transition series is present in the 4th period, and starts after Ca (Z = 20) of group 2 with the configuration [Ar]4s², or scandium (Sc), the first element of group 3 with atomic number Z = 21 and configuration [Ar]4s¹3d¹, depending on the definition used. As we move from left to right, electrons are added to the same d subshell till it is complete. The element of group 11 in the first transition series is copper (Cu) with an atypical configuration [Ar]4s¹3d¹⁰. Despite the filled d subshell in metallic copper it nevertheless forms a stable ion with an incomplete d subshell. Since the electrons added fill the (n – 1)d orbitals, the properties of the d-block elements are quite different from those of s and p block elements in which the filling occurs either in s or in p orbitals of the valence shell. The electronic configuration of the individual elements present in all the d-block series are given below:



First (3d) d-block Series (Sc–Zn)

Group	3	4	5	6	7	8	9	10	11	12
Atomic number	21	22	23	24	25	26	27	28	29	30
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electron configuration	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$

Second (4d) d-block Series (Y–Cd)

Atomic number	39	40	41	42	43	44	45	46	47	48
Element	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Electron configuration	$4d^15s^2$	$4d^25s^2$	$4d^45s^1$	$4d^55s^1$	$4d^55s^2$	$4d^75s^1$	$4d^85s^1$	$4d^{10}5s^0$	$4d^{10}5s^1$	$4d^{10}5s^2$

Third (5d) d-block Series (Lu–Hg)

Atomic number	71	72	73	74	75	76	77	78	79	80
Element	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Electron configuration	$5d^16s^2$	$5d^26s^2$	$5d^36s^2$	$5d^46s^2$	$5d^56s^2$	$5d^66s^2$	$5d^76s^2$	$5d^96s^1$	$5d^{10}6s^1$	$5d^{10}6s^2$



Fourth (6d) d-block Series (Lr–Cn)										
Atomic number	103	104	105	106	107	108	109	110	111	112
Element	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
Electron configuration	$7s^2 7p^1$	$6d^2 7s^2$	$6d^3 7s^2$	$6d^4 7s^2$	$6d^5 7s^2$	$6d^6 7s^2$	$6d^7 7s^2$	$6d^8 7s^2$	$6d^9 7s^2$	$6d^{10} 7s^2$

A careful look at the electronic configuration of the elements reveals that there are certain exceptions to the Madelung rule. For Cr as an example the rule predicts the configuration $3d^4 4s^2$, but the observed atomic spectra show that the real ground state is $3d^5 4s^1$. To explain such exceptions, it is necessary to consider the effects of increasing nuclear charge on the orbital energies, as well as the electron–electron interactions including both Coulomb repulsion and exchange energy.

IV. CONCLUSIONS

Stability of poly(pyrazolyl)borates complexes with the studied transition metals is controlled by the steric effects of the substituents. [HB(3-Mepz)3] - and [B(3-Mepz)4] - extract all the studied metal ions at a higher pH compared with [HB(pz)3] - and [B(pz)4] - , respectively. For [B(3-iPrpz)4] - , since isopropyl groups hinder complex formation with Co²⁺ in a tridentate fashion, the bidentate complex is formed. It is expected that the determination of the structures of the complexes of [HB(3- iPrpz)3] - and [B(3-iPrpz)4] - by X-ray crystallography will give insights into selectivity of these ligands.

REFERENCES

1. Y. Sohrin, H. Kokusen, S. Kihara, M. Matsui, Y. Kushi and M. Shiro, J. Am. Chem. Soc., 1993, 115, 4128.
2. Y. Sohrin, M. Matsui, Y. Hata, H. Hasegawa and H. Kokusen, Inorg. Chem., 1994, 33, 4376.
3. H. Kokusen, Y. Sohrin, M. Matsui, Y. Hata and H. Hasegawa, J. Chem. Soc., Dalton Trans., 1995, 195.
4. S. Trofimenko, J. Am. Chem. Soc., 1967, 89, 3170.
5. K. Niedenzu, P. M. Niedenzu and K. R. Warner, Inorg. Chem., 1985, 24, 1604.
6. S. Trofimenko, J. C. Calabrese and J. S. Thompson, Inorg. Chem., 1987, 26, 1507.
7. T. Kitano, Y. Sohrin, Y. Hata, H. Kawakami, T. Hori and K. Ueda, J. Chem. Soc., Dalton Trans., 2001, submitted.
8. N. Walker, D. Stuart, Acta Crystallogr., Sect. A, 1983, 39, 158.
9. G. M. Sheldrick, in “Crystallographic Computing”, ed. G. M. Sheldrick, C. Kruger and R. Goddard, 1985, Vol. 3, Oxford University Press, Oxford, England, 175.
10. M. C. Burla, M. Camalli, Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, J. Appl. Crystallogr., 1989, 22, 389.
11. A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, J. Appl. Crystallogr., 1994, 27, 435.
12. P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, “The DIRDIF94 program system, Technical Report of the Crystallography Laboratory”, University of Nijmegen, The Netherlands, 1994.
13. S. Calogero, G. G. Lobbia, P. Cecchi, G. Valle and J. Friedl, Polyhedron, 1994, 13, 87.
14. C. Santini, C. Pettinari, M. Pellei, G. G. Lobbia, A. Pifferi, M. Camalli and A. Mele, Polyhedron, 1999, 18, 2255.
15. D. L. Reger, S. S. Mason, A. L. Rheingold and R. L. Ostrander, Inorg. Chem., 1993, 32, 5216.
16. R. D. Shannon, Acta Crystallogr., Sect. A 1976, 32, 751. 17. A. Bondi, J. Phys. Chem., 1964, 68, 441.



INNO SPACE
SJIF Scientific Journal Impact Factor
Impact Factor: 8.118



ISSN INTERNATIONAL
STANDARD
SERIAL
NUMBER
INDIA



INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

 **9940 572 462**  **6381 907 438**  **ijirset@gmail.com**



www.ijirset.com

Scan to save the contact details